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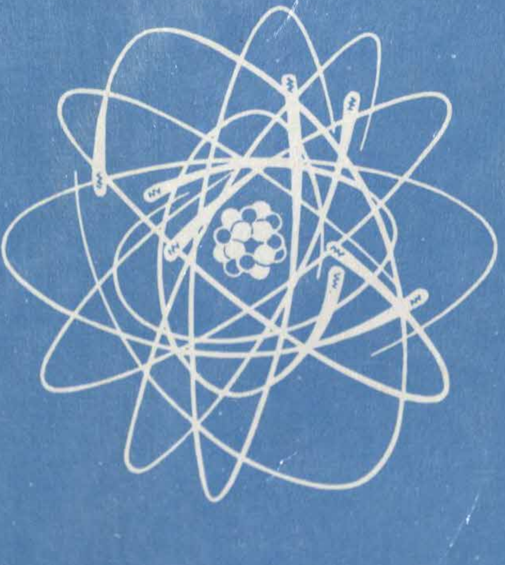
ELEMENTS OF CHEMISTRY

MAITY • GANGULY



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CONSTITUTION OF INDIA

PREAMBLE

WE, THE PEOPLE OF INDIA, having solemnly resolved to constitute India into a SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC and to secure to all its citizens ;

JUSTICE, social, economic and political ;

LIBERTY of thought, expression, belief, faith and worship ;

EQUALITY of status and of opportunity

and to promote among them all ;

FRATERNITY assuring the dignity of the individual and the unity and integrity of the Nation ;

IN OUR CONSTITUENT ASSEMBLY this twenty-sixth day of November, 1949, do HEREBY ADOPT, ENACT AND GIVE TO OURSELVES THIS CONSTITUTION.

ভারতীয় সংবিধান

প্রস্তাবনা

"আমরা, ভারতের জনগণ, ভারতকে সার্বভৌম, সমাজতান্ত্রিক, ধর্মনিরপেক্ষ, গণতান্ত্রিক সাধারণতন্ত্র রূপে গড়ে তুলতে এবং তার সকল নাগরিকই যাতে সামাজিক, অর্থনৈতিক ও রাজনৈতিক ন্যায়বিচার, চিন্তা, মতপ্রকাশ, বিশ্বাস, ধর্ম এবং উপাসনার স্বাধীনতা, সামাজিক প্রতিষ্ঠা অর্জন ও সুযোগের সমতা প্রতিষ্ঠা এবং তাদের সকলের মধ্যে ব্যক্তির মর্যাদা এবং জাতীয় ঐক্য ও সংহতি সুনিশ্চিতকরণের মাধ্যমে তাদের মধ্যে যাতে ভ্রাতৃত্বের ভাব গড়ে ওঠে তার জন্য সত্যনিষ্ঠার সঙ্গে শপথ গ্রহণ করে, আমাদের গণপরিষদে আজ, ১৯৪৯ সালের ২৬শে নভেম্বর, এতদ্দ্বারা এই সংবিধান গ্রহণ, বিধিবদ্ধ এবং নিজেদের অর্পণ করছি।"

Written according to the syllabuses of Chemistry for the Plus-two
Courses of Classes XI &XII

ELEMENTS OF CHEMISTRY

[PART I]

[For H.S., Jt. Ent. & I. I. T. Entrance Examinees]

by

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Preface to the First Edition

On repeated requests by our friends and welwishers along with our beloved students we took pains to bring out this book on Chemistry in English version. We tried our best to update this book in every respect keeping in mind the warm reception accorded to our chemistry book written in Bengali *'Rasayan'*, Vol I and Vol II. This book is compiled for the students appearing at the entrance examinations for engineering and medical courses, in addition to +2 course of different Boards and Higher Secondary Councils of other states of India.

This volume consists of two parts—the first part is devoted to General and Physical Chemistry and the second part deals with the Inorganic Chemistry (non metals).

The salient features of this book are—

(i) It fulfils the needs of those students who wish to have a sound conceptual knowledge of the subject in the most easy and simple method.

(ii) This book is of great importance to the students appearing for the Higher Secondary Examination, J.E.E., I.I.T Entrance, N.T.S.E., N.DA. and for other competitive examinations on all India basis. This book will help the students to have an idea of what types of questions they can expect in different competitive examinations.

(iii) Every chapter of this book is well-equipped with all types of questions set in the last ten years of I.I.T, J.E.E and other important entrance examinations. Within each chapter, questions have been grouped according to their type e.g., short notes on, conversions, distinguish between, preparation and properties, what happens when, explain why, removal of impurities, problems on identifications etc. In addition to this, a large number of objective type questions, short answer type questions are added at the end of every chapter. Solving of these questions will bring confidence in the students and they will be in a position to answer any other allied questions on the topic.

(iv) In every chapter of physical chemistry there is theoretical discussion followed by different types of numerical problems.

(v) Revision charts have been given on the preparation and properties of important compounds and elements.

(vi) Visual aids leave a deep impression on young minds and so this book has been abundantly illustrated with neat diagrams.

(vii) Only a fairly detailed study of informative matters of inorganic chemistry enables the students to appreciate the problems. Here we have tried to accommodate details of factual part as far as possible. But too much irrelevant informations make the brain fatigue and disinterests the students to the subject.

Consequently theoretical aspects of facts have been incorporated whereever possible so that the students need not depend too much on memory.

In composing this book we have freely consulted a number of books written by foreign and Indian authors so that the students can get the correct and up-to-date informations in shortest possible time.

We are confident that the way of presentation in this book will help our students to read the subject with much interest and pleasure without giving any pressure to memory.

Inspite of our best efforts, we do not claim that the present book is free from errors. We shall feel highly obliged if these are brought to our notice. Suggestions for the improvement of the book will be gratefully acknowledged.

Our sincerest thanks are due to the respected teachers of various schools and colleges and especially to Dr. Murari Mohan Lahiri, Head of the Department of Chemistry, Belur Ramkrishna Mission College, who helped us by their valuable suggestions in composing this book. We express our sincere thanks to the members of the efficient staff of M/s Publishing Syndicate for their sincere help in bringing out this book.

Last but not the least, we wish to put in black and white, our warmest thanks and sincere gratitude to Sri Sachchidananda Guha, the most dynamic personality and very efficient 'captain' of Publishing Syndicate team and we must confess that this book finally comes to light only because of his constant inspiration, untiring effort and encouragement.

Sukhendu Maity

16.6.95. **Manas Ganguly**

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FOR ADMISSION TO ENGINEERING, MEDICAL AND
TECHNOLOGICAL DEGREE COLLEGES

SYLLABUS FOR CHEMISTRY

FULL MARKS 100

Each module carries 10 marks

MODULE 1

A. Atomic Structure

Fundamental particles of atom—their discovery.

Structure of atom. Rutherford model—its strong and weak points. Bohr's atomic model—its advantages and limitations. Distribution of electrons in shells and sub-shells. Orbits and orbitals. Mass number of atoms. Atomic number.

B. Radioactivity and atomic nucleus

Definition of radioactivity. Theory of radioactive disintegration. Difference between radioactive disintegration and chemical transformation. Artificial radioactivity. Isotopes. Applications of radioactivity.

C. Periodic classification of elements

Mendeleeff's periodic law. Periodic Table. Significance of groups and sub-groups. Strong and weak points of Mendeleeff's Periodic Table. Modern Periodic Table—classification of elements on the basis of electronic configuration. Variation of electronegativity across the Periodic Table.

MODULE 2

A. Laws of chemical combination

Statement of the laws and experimental verification. Gay Lussac's law of gaseous volumes. Postulates of Dalton's atomic theory. Merits and limitations of Dalton's atomic theory. Interpretation of the laws of chemical combination in terms of Dalton's atomic theory. Concept of atomic weight.

B. Avogadro's hypothesis and molecules

Factors that led to the adoption of Avogadro's hypothesis. Concept of molecule. Statement of Avogadro's hypothesis. Role of Avogadro's hypothesis in reconciling Gay Lussac's law with Dalton's atomic theory. Derivation of the law of gaseous volumes from Avogadro's hypothesis. Modification of Dalton's atomic theory in the light of concept of molecules. Concepts of molecular weight, gram molecular weight, molar volume, and Avogadro's number. Determination of Avogadro's number. Important deductions from Avogadro's hypothesis. Concept of mole.

C. Chemical equations and valency

Definition of valency. Valency of elements and radicals. Variable valency. Meaning of a chemical equation. Limitation of a chemical equation. Types of chemical reaction. Chemical calculations—calculation involving weight to weight, weights and volumes. Eudiometry. Empirical formula and molecular formula.

D. Nature of chemical bond

Electronic theory of valency. Electrovalency. Conditions of formation of ionic bond. Examples of ionic bonding. Characteristics of ionic compounds. Covalency. Lewis electron-dot structure. Formation of covalent bond. Valence bond theory. Hybridisation. Characteristics of covalent compounds. Coordinate bond. Polarity of covalent bonds. Dipole moment. Hydrogen bond.

MODULE 3

A. Properties of gases

Volume-pressure relation of a gas. Temperature-volume relation of a gas. Absolute temperature and absolute zero. Combination of Boyle's law and Charles' law. Molar gas constant. Dalton's law of partial pressure. Partial pressure and mole fraction. Diffusion of gases—Graham's law. Real gases—deviation from behaviour of ideal gases. Numerical problems (For ideal gases only).

B. Solutions and solubility

Characteristics of solutions. Comparison of solution and compound. Classification of solutions according to concentration. Solubility. Determination of solubility. Dependence of solubility on temperature and pressure. Solubility curve. Crystallisation. Water of crystallisation. Determination of water of crystallisation. Suspension, colloidal state and true solution. Purification of colloids. Practical applications of colloids. Numerical problems.

C. Equivalent weight and atomic weight

Equivalent weight of an element. Gram equivalent weight. Equivalent weight of radicals. Relation between atomic weight and molecular weight. Methods of determination of equivalent weight of elements. Determination of atomic weight of elements. Determination of molecular weight by Victor Mayer's method. Mitscherlich's law of isomorphism.

D. Acids, Bases and Salts

Arrhenius' concept of acids. Classification of acids. Arrhenius' concept of bases. Classification of bases. Salts and their classification. Oxides and their classification. Equivalent weight of acid, base and salt. Concentration of a solution. Neutralisation. Standard solution—definition, characteristics, examples. Indicators—definition, types, selection. Numerical problems on acidimetry and alkalimetry.

MODULE 4

A. Oxidation and reduction

Classical concepts of oxidation and reduction. Electronic concept of oxidation and reduction. Relation between old and new concepts. Oxidation state or oxidation number. Oxidation number and valency, rules for balancing chemical equations by oxidation number method. Equivalent weights of oxidants and reductants.

B. Electrolysis

Electrical conductivity of melts and aqueous solutions. Definition of electrolysis. Comparison between thermal and electrolytic dissociation. Arrhenius' theory of electrolytic dissociation. Faraday's laws of electrolysis. Electrochemical equivalent. Relation between chemical equivalent and electrochemical equivalent of an element (Numerical problems on electrolysis).

C. Chemical equilibrium

Definition. Law of mass action. Concept of chemical equilibrium. Equilibrium constants K_p, K_c. Le Chatelier's principle and its application. (Numerical problems on law of mass action excluded.)

Physico-chemical principles of large scale preparation of hydrogen, ammonia, nitric acid, sulphuric acid (contact process only) and coal gas (details of preparation to be omitted).

D. Catalysts and Catalysis

Homogeneous and heterogeneous catalysis, autocatalysis, positive and negative catalysts, promoters and catalyst poison (Definitions and examples only).

MODULE 5

A. Chemistry of oxygen, hydrogen, water, hydrogen peroxide and ozone

Preparation of oxygen from potassium chlorate, oxides of weak electropositive metals, nitrates of metals; by decomposition of compounds rich in oxygen; from oxy-acids : concentrated nitric and sulphuric acids; from hydrogen peroxide and peroxide compounds; by electrolysis of water; from air. Formation of oxides. Oxidising property of oxygen. Reducing action of oxygen. Absorption of oxygen.

Preparation of hydrogen in the laboratory; from acids, alkalis and water. Properties of hydrogen—reducing property, oxidising property, action on non-metals. Occlusion of hydrogen, nascent hydrogen (excluding explanation). Atomic hydrogen. Ortho and para-hydrogen. Isotopes of hydrogen.

Hard and soft water, causes of hardness of water. Softening of hard water by boiling; by Clarks process; by lime soda process, permutit process, ion exchange resin process; demineralisation of water. Degree of hardness. Principles of determination of composition of water by Dumas' and Morley's methods. Heavy water.

Hydrogen peroxide. Laboratory method of preparation. Merck's process. Large scale preparation of hydrogen peroxide by electrolytic and auto oxidation processes. Properties of hydrogen peroxide—acid property, oxidising property, reducing property. Tests of hydrogen peroxide. Strength of hydrogen peroxide.

Laboratory method of preparation of ozone. Preparation of ozone from ozonised oxygen. Oxidising property of ozone. Reaction of ozone with peroxides. Tests for ozone. To show that oxygen and ozone are allotropes of the same element.

B. Nitrogen and its compounds

Laboratory method of preparation of nitrogen. Preparation of nitrogen from nitrogenous compounds. Action of nitrogen on metals and non-metals.

Laboratory method of preparation of ammonia. Other methods. Manufacture of ammonia by Haber process. Action of ammonia on metallic salt and chlorine. Formation of complex salts of ammonia. Nessler's reagent.

Laboratory method of preparation of N_2O, NO, N_2O_4, HNO_2 and HNO_3. Industrial method of preparation of HNO_3. Action of HNO_3 on non-metals, copper and zinc. Aqua regia. Oxidising property of HNO_3. Oxidising and reducing action of HNO_2. Detection of nitrites and nitrates independently and in presence of each other.

C. Boron and its compounds

Preparation of boron. Reaction with air. Action on acids and alkalis. B_2O_3 is amphoteric—why? Action of B_2O_3 on concentrated H_2SO_4 and CaF_2 or KBF_4. Preparation of boric acid from borax and colemanite. Action of boric acid on NH_4HF. Titration of boric acid. Tests for boric acid. Preparation of borax. Borax bead test.

D. Carbon and its compounds

Allotropic modifications of carbon. Preparation of CO. Carbogen. Action of CO on nickel. Production of organic compounds. Detection of CO. Preparation of CO_2. Action of CO_2 on lime water, ammonia. Combustibility of CO_2. Dry ice. Fire extinguisher. Coalgas. (Details of preparation omitted).

MODULE 6

A. Phosphorus and its compounds

Preparation of white phosphorus from bone ash (by old retort process and Parker-Robinson process). Conversion of red phosphorus to white phosphorus and vice versa. Properties of phosphorus—chemiluminescence, reaction with hot concentrated HNO_3, concentrated alkali, $CuSO_4$ and $AgNO_3$ solutions, acidified KIO_3 solution. Structure of white and red phosphorus—dependence of their properties on structure.

Preparation of phosphene. Action of phosphene on chlorine, $CuSO_4$ and $AgNO_3$. Holmes' signal. Ammonia is a much stronger base than phosphene—explanation. Phosphorus trioxide—reaction with hot water and alkalis.

Phosphorus pentoxide—reaction with water and alkalis. Action as a dehydrating agent.

Phosphorus trichloride and pentachloride—hydrolysis.

H_3PO_3—preparation; reaction with $CuSO_4$, $AgNO_3$ and $HgCl_2$. A strong reducing agent—explanation. Na_2HPO_3 a normal salt—explanation.

H_3PO_4—preparation from bone ash. Action of heat. Reaction with alkali. Action on bromides. Identification of the phosphatic radical. Microcosmic salt bead test.

B. Halogens

Fluorine as a 'superhalogen'. Difficulties in isolation of fluorine. Preparation of fluorine by Moissan, Dennis, and Whytlaw and Gray methods—electrolytic cell, electrodes, electrolytes, reactions at electrodes. Reaction with water, alkalis and organic compounds. Oxidising property. Tests for fluorides.

Preparation of chlorine : action of acids on metallic chlorides. Preparation at room temperature. Action of chlorine on alkali, dry slaked lime, quick lime, H_2O_2. Bleaching property (comparison with SO_2).

Preparation of bromine : action of acids on bromides. Detection of bromides and iodides individually when they are associated together. Chromyl-chloride test.

Preparation of HF, anhydrous HF, HBr and HI. HI is a stronger reducing agent than HCl and HBr.

C. Sulphur and its compounds

Allotropes of sulphur. Action of acids, alkalis and K_2CO_3 on sulphur. Preparation of H_2S, SO_2, SO_3, H_2SO_3 and H_2SO_4. Reducing action of H_2S and SO_2. Oxidising property of SO_2. Action of H_2SO_4 on metals and non-metals. Tests for sulphates and sulphites. Application of H_2S in qualitative analysis of basic radicals.

MODULE 7

A. General metallurgical processes

Ores, minerals and gangue—definition. Flux and slag. Metallurgical processes—concentration, calcination, roasting, smelting and reduction. Refining. General methods of reduction—carbon reduction, self reduction, hydrometallurgy, electrolytic reduction, thermal reduction. Principles of thermal refining and electrolytic refining.

Principles of extraction of

(a) Sodium—by Castner's process and Down's process. Comparison between two processes.
(b) Calcium—by electrolytic reduction, thermal reduction.
(c) Aluminium—by Bayer's process, Hall's process, Serpeck's process, electrolytic reduction. Electrolytic refining.
(d) Copper—by dry process, wet process. Refining.
(e) Zinc—by carbon reduction process, electrolytic reduction process. Refining.
(f) Iron—manufacture of cast iron by carbon reduction process. Manufacture of steel from cast iron by Bessemer process, open hearth process.

B. Compounds of metals

Principles of preparation, properties and uses of oxides, hydroxides, chlorides, nitrates, sulphates and carbonates of the above metals.

C. Large scale production of important compounds

Principles of large scale preparation of caustic soda, washing soda, sodium bicarbonate, bleaching powder, plaster of paris, common alum, blue vitriol, white vitriol, green vitriol.

MODULE 8

A. Electronic structure of organic compounds

Electronic configuration of carbon. Theory of structure of organic compounds—constant tetravalency of carbon. Structure or organic compounds according to tetrahedral model. Modern concept of sigma bond, pi bond and hybridisation of orbitals. Isomerism—structural isomerism, stereoisomerism. (Types and examples only). I.U.P.A.C. nomenclature of organic compounds.

B. Saturated hydrocarbons

General methods of preparation—by decarboxylation of carboxylic acids; reduction of alkyl halides; catalytic hydrogenation; Wurtz reaction; Kolbe's synthesis; reduction of carbonyl compounds; reduction of alcohols, aldehydes, ketones and carboxylic acids.

General properties—halogenation; nitration; sulphonation; oxidation—combustion; pyrolysis; isomerisation; aromatisation; dehydrogenation.

Methane—principles of preparation; properties.

Ethane—principles of preparation; properties.

C. Unsaturated hydrocarbons

General methods of preparation—by dehydration of alcohols, dehydro-halogenation of alkyl halides, Kolbe's electrolytic method, partial halogenation of alkynes, pyrolysis; from Grignard reagent; by heating quaternary ammonium hydroxide.

General properties. Reaction—combustion, addition reaction, ozonolysis, polymerisation, isomerisation; substitution reaction with halogens.

Ethylene—principles of preparation; properties.

D. Halogen derivatives of paraffins

General methods of preparation. General properties. Preparation and properties of chloroform and iodoform.

E. Aliphatic alcohols

Preparation of methyl alcohol by destructive distillation of wood; from water gas, natural gas, from methyl chloride, methyl acetate, methyl amine and formaldehyde.

Properties of methyl alcohol. Reaction with alkali metals, carboxylic acids, halogen. Halogenation, dehydration, oxidation, reduction.

Preparation of ethyl alcohol from glucose, molasses, starch. Properties of ethyl alcohol.

Reaction with alkali metals, carboxylic acids, halogen acids, ammonia. Halogenation, dehydration, oxidation, reduction. Haloform reaction. Chemical tests to distinguish methanol from ethanol, chloroform from ethanol, chloroform from methanol.

Interconversions—from higher alcohol to lower alcohol and vice versa; from primary alcohol to secondary or tertiary alcohol and vice versa; methanol and ethanol into formaldehyde and formic acid; methanol and ethanol into methane, ethylene and acetylene; ethanol into ethane and propane etc.

MODULE 9

A. Ethers and carbonyl compounds

Preparation of ether by dehydration of alcohols; by Williamson synthesis; by heating alkyl halides with silver oxide; by the action of diazomethane on alcohols.

General properties. Reactions—formation of peroxides, oxonium salts; halogenation; reaction with H_2SO_4, PCl_5, HI, acid chlorides, CO; combustion.

Diethyl ether—preparation, properties.

Chemical tests to distinguish between ether and methanol; preparation of aldehydes and ketones by oxidation of alcohols, catalytic dehydrogenation of alcohols, oxidation of alkenes, reduction of acid chlorides, hydrolysis of gem-dihalides, heating calcium salts of fatty acids; by Stephen reduction, hydrolysis of aceto-acetic ester; from Grignard reagent. General properties. Reactions—oxidation, reduction, addition; reaction with alcohol, ammonia derivatives, halogens; aldol condensation; Cannizzaro's reaction; haloform reaction.

Formaldehyde, acetaldehyde, acetone—preparation. Properties.

B. Aliphatic acids

General methods of preparation—by oxidation of primary alcohols and aldehydes, oxidation of secondary alcohols and ketones, hydrolysis of nitrites or alkyl cyanides, hydrolysis of esters, hydrolysis of acid chlorides and acid anhydrides, hydrolysis of acid amides, carboxylation of alkenes, by haloform reaction; from sodium alkoxides.

Properties. Reactions—replacement of ionic hydrogen, replacement of hydroxyl group, reactions of carbonyl group, decarboxylation, replacement of hydrogen atom of alkyl group by halogens; dehydration.

Formic acid, acetic acid, oxalic acid—preparation. Properties.

C. Acid derivatives

Acetyl chloride, acetic anhydride, acetamide, amines, nitrites—preparation. Properties.

MODULE 10

A. Aromatic compounds

Isolation of aromatic compounds from coal tar.

Benzene—preparation. Properties. Reactions—halogenation, sulphonation, nitration; Friedel Craft reaction; chlorination, hydrogenation, ozonolysis; combustion, oxidation, aldehyde synthesis, chloromethylation.

Toluene—Preparation. Properties. Reactions—chlorination, oxidation, hydrogenation, nitration, sulphonation; Friedel Craft reaction.

B. Nitrobenzene

Preparation from benzene, diazonium salts, aniline. Properties—reduction, halogenation, nitration, sulphonation.

C. Aniline

Preparation from nitrobenzene, chlorobenzene, phenol, benzamide, benzene, azo compounds. Properties—reaction with acids, alkyl halides. Carbylamine reaction, benzoylation, diazo reaction. Conversions using diazonium salts.

D. Phenol

Preparation from coal tar, benzene, benzene diazonium chloride, chlorobenzene, aniline. By Raschig process.

Properties—reaction with NaOH, Zn, PCl_5, P_2S_5, NH_3. Acetylation, benzoylation. Reduction. Reaction with Br_2. Nitration, sulphonation, nitrosation. Friedel Craft reaction, Kolbe Schmidt reaction, Gattermann reaction. Condensation reaction. Reaction with phthalic anhydride. Oxidation. Uses.

CONTENTS

• PHYSICAL CHEMISTRY •

CHAPTERS PAGES

INTRODUCTION ... ... 1—8

1. STOICHIOMETRY ... ... 9—44

Law of conservation of mass or law of indestructibility of matter 9 The law of definite or constant proportions 13 Law of multiple proportions 15 The law of Reciprocal or equivalent proportions 18 Gay Lussac's law of gaseous volumes 22 Worked out examples 23 Dalton's atomic theory—Constitution of matter 35 Utility of Dalton's atomic theory 35 Limitations of Dalton's atomic theory 36 Explanations of the Laws of Stoichiometry in the light of Dalton's 37 Concept of atomic weight or atomic mass 38 Atomic mass unit or a.m.u. 40 *Physical and chemical scales of atomic weight 40* Atomic-molecular theory 41 Exercises 41.

2. AVOGADRO'S HYPOTHESIS AND MOLECULES ... 45—84

Introduction to Avogadro's hypothesis 45 Modification of dalton's atomic theory in the light of Avogadro's Molecular Theory 48 Concept of Molecular Weight 49 Gram molecule or Gram molecular weight or gram mole 50 Gram molecular volume or molar volume 50 Avogadro's Number 51 Applications of Avogadro's hypothesis and its important deductions 53 Importance of Avogadro's hypothesis in chemistry 61 Concept of Mole 62 Problems on Avogadro's hypothesis 63 Exercises 81

3. CHEMICAL EQUATION AND VALENCY ... ... 85—139

Symbol and formula 85 Valency 86 Writing of correct formula of compounds 98 Structural formula 90 Chemical equations 91 Significance of a chemical equation 92 Methods of balancing chemical equation 94 Types of chemical reactions 98 Chemical calculations 100 Examples 101 Eudiometry 115 Numerical problems 118 Emperical formula and molecular formula 130 Numerical examples 131 Exercises 135

4. EQUIVALENT WEIGHT AND ATOMIC WEIGHT ... 140—179

Introduction 140 Equivalent weight of an element 142 Electronic approach 146 Different methods of the determination of equivalent weights of elements 147 Determination of atomic weight of element 156 *Mass spectograph method 162* Determination of Molecular weight of a substance 163 *Beckmann's process 164 Raoult's law of relative lowering of vapour pressure 164* Determination of Molecular weight by Victor Meyer's method 165 Numerical examples 167 Exercises 177

5. ACIDS, BASES AND SALTS ... ... 180—200

Acids 180 Properties of acids 181 Classification of acids 182 Base 185 Alkali 186 Properties of Bases and Alkalis 186 Classification of Bases 187 Salts 192 Classification of salts 193 Oxides 195 Exercises 199

6. ACIDIMETRY AND ALKALIMETRY ... ... 201—246

Equivalent Weight of Acid, Base and Salt 201 Concentration of a solution 203 Conversion of strength of solution from one unit to other 209 Neutralisation 211 Standard solution 213 Preparation of Primary standard solution of (N/10) Na_2CO_3 214 Preparation of Secondary standard solution 215 Titration Process 216 Indicators 217 A few Principles of Acidimetry and alkalimetry 219 Numerical examples 219 Exercises 243

7. PROPERTIES OF GASES ... ... 247—287

Special properties of gases 247 State Variables 247 Volume-Pressure relation of a gas—Boyle's law 248 Temperature-Volume relation of a gas—Charles' Law 250 Absolute temperature and Absolute zero 251 Charle's Law and Absolute scale of temperature—alternative statement of Charle's law 252 Combination of Boyle's law and Charles' law

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N.B. Topics in *italics* are not included in W.B.H.S. Syllabi.

253 Partial pressure and Dalton's law of partial pressure 257 Relation between partial pressure and mole fraction 259 *Amagat's law of Partical Volume 260 Kinetic theory of gases 261* Diffusion of gases 264 Effusion of gas 267 *Real gases-deviation from the behaviour of ideal gas 269 Vander Waal's equation 270 Application of Vander Waal's equation 271* Numerical problems on gas laws 271 Exercises 283

8. SOLUTION AND SOLUBILITY ... ... 288—335

Solution 288 Similarities and dissimilarities between solution and compound 289 Classification of solution according to concentration 290 State of equilibrium between the solvent and solute in a solution 292 *Mechanism of dissolution of a solute in a liquid—Water is a versatile solvent 293* Solubility 296 *Determination of solubility 296* Influence of temperature and pressure on the solubility of solids in liquids 298 Solubility curve 298 *Effect of pressure on a solution of a gas in a liquid 301 Vapour pressure of solutions and Raoult's law 302 Solution of Non-volatile solute 303 Colligative properties of solution 304 Osmotic pressure, association and ionisation of solute 307* Crystals, crystalline and amorphous substance 308 Uses of crystallisation 309 Water of crystallisation 310 Determination of water of crystallisation of blue vitriol 311 Efflorescence and Efflorescent substance 312 Deliquescence and Deliquescent substance 312 Colloids 314 Suspension, colloidal solution and true solution 314 Problems on solubility of matter 325 Exercises 333

9. ELECTROLYSIS ... ... 336—380

Electrolytes 336 Electrolysis 337 Thermal dissociation and Electrolytic dissociation 337 Arrhenius theory of electrolytic dissociation 338 Anions and Cations conduct electricity in the same direction 342 Factors influencing electrolysis 345 Examples of electrolysis 348 Some important facts about electrolysis 351 Practical units of electric current and quantity of electricity 352 Faraday's laws of electrolysis 352 Charge of 1 gram-ion = 1 Faraday 358 Relation among Faraday, Avogadro number and the charge of an electron 359 Practical applications of electrolysis 361 Numerical problems 363 Exercises 376

10. CHEMICAL EQUILIBRIUM AND LAW OF MASS ACTION ... 381—423

Concept of reversible reaction 381 Reversible reaction 382 Chemical equilibrium 383 Characteristics of chemical equilibrium 385 Law of mass action 387 Equilibrium constant 388 *Relation between K_p and K_c 389 Relation between K_p and K_x 391* Characteristics of equilibrium constant (K) 391 Types of chemical equilibrium 393 Importance of equilibrium constant 393 *Applications of law of mass action—Determination of equilibrium constant of a few reactions 395* Le·Chatelier's principle 398 Application of Le Chatelier's principle in the manufacturing process 406 *Le Chatelier's principle in physical equilibrium 409* All reactions are reversible 411 Some special problems solved 411 Numerical examples 415 Exercises 420

11. IONIC EQUILIBRIA ... ... 424—457

Electrolytes 424 Degree of dissociation or degree of ionisation (α) 424 Ostwald's dilution law 425 Ionic product of water (Kw) 425 pH and pOH 426 Buffer solution 428 Hydrolysis of salts 431 Indicators 437 Solubility product 441 Numerical problems 447 Exercises 455

12. CONDUCTANCE ... ... 458—470

Conductance of solution—electrolytic conductance 458 Specific conductance 459 Equivalent conductance 459 Molar conductance 460 Measurement of conductance 461 Variation of equivalent conductance with concentration 462 Equivalent conductance at infinite dilution λ_0 462 Kohlrausch's law of independent migration of ions 463 Ionisation of weak electrolyte—degree of dissociation 463 Ionic mobility 464 Transport number 464 Solubility and equivalent conductance 465 Numerical problems 465 Exercises 468

N.B. Topics in *italics* are not included in W.B.H.S. Syllabi.

APPENDIX ... ... 471—473

• INORGANIC CHEMISTRY •

1. OXYGEN, HYDROGEN, WATER, HYDROGEN PEROXIDE AND OZONE ... ... 1—86

Preparation of Oxygen 2 Other methods of preparation of Oxygen 4 Properties of Oxygen 9 Experiments to illustrate some important properties of Oxygen 11 Uses of Oxygen 13 Catalyst and Catalysis 13 *The position of hydrogen in the periodic table 18* Preparation of hydrogen 19 Hydrogen produced in Kipp's apparatus 22 Other methods of preparation of hydrogen 22 Large scale preparation of hydrogen 24 Properties of hydrogen 27 Nascent hydrogen 29 Allotropy of hydrogen—Ortho and para hydrogen 33 Isotopes of hydrogen 34 Natural sources of water 38 Hard water and soft water 39 Removal of hardness of water 40 *Estimation of hardness—degree of hardness of water 45* Purification of drinking water 49 Properties of water 50 *Composition of water 54* Heavy water or Deuterium Oxide 59 Preparation of hydrogen peroxide 59 Other methods of preparation of hydrogen peroxide 62 Large scale preparation of hydrogen peroxide 62 Properties of hydrogen peroxide 64 Uses of hydrogen peroxide 72 Preparation of Ozone 73 Properties of Ozone 75 Uses of ozone 80 Exercises 82

2. AIR, NITROGEN AND ITS COMPOUNDS ... ... 87—143

Constituents of air 87 Experiment to prove the presence of nitrogen in air 88 Composition of air 89 Air is a mechanical mixture and not a chemical compound 90 Comparison of nitrogen with the other members of group VB 91 Laboratory method of preparation of nitrogen 92 Other methods of preparation of nitrogen 93 Properties of nitrogen 95 Nitrogen cycle in nature 97 Fixation of nitrogen 98 Preparation of ammonia 100 Other methods of preparation of ammonia 101 Properties of ammonia 102 Uses of ammonia 105 Experiments to illustrate some important properties of ammonia 105 Large scale preparation of ammonia—Haber's process 108 Nitrous oxide or Laughing gas (N_2O) 111 Nitric oxide (NO) 114 Nitrogen dioxide $\rightleftharpoons$ Dinitrogen tetroxide [$2NO_2 \rightleftharpoons N_2O_4$] 116 Dinitrogen pentoxide (N_2O_5) 119 Nitrous acid (HNO_2) 120 Nitric acid (HNO_3) 123 Large scale preparation of nitric acid 135 Exercises 140

3. BORON AND ITS COMPOUNDS ... ... 144—156

Occurrence of Boron 144 Preparation of Boron 144 Properties of Boron 145 Boric acid 147 Borax or Sodium Pyroborate or Sodium tetra borate 149 Exercises 155

4. CARBON AND ITS COMPOUNDS ... ... 157—191

Occurrence 157 Characteristics of Carbon atom 158 Allotropy and allotropic modifications of elements 158 Allotropy of Carbon 159 Carbon monoxide 168 Carbon di-oxide 174 Carbonic acid 182 *Metallic carbonates 183 Metallic bi-carbonates 183* Fuels—Coal gas 184 Exercises 188

5. PHOSPHORUS AND ITS COMPOUNDS ... ... 192—225

Occurrence of phosphorus 192 Preparation of white phosphorus 192 Allotropy of phosphorus 195 Properties of white and red phosphorus 196 Uses of phosphorus 199 Structure of white and red phosphorus 199 Preparation of phosphine 202 Other methods of preparation of phosphine 203 Properties of phosphine 204 Uses of phosphine 205 Comparison between phosphine and ammonia 207 Phosphorus trioxide (P_2O_3 or P_4O_6)—anhydride of phosphorus acid 208 Phosphorus pentoxide [P_2O_5 or P_4O_{10}] 209 Oxyacids of phosphorus 213 *Pyrophosphoric acid 219 Metaphosphoric acid 220* Justification of placing nitrogen and phosphorus in the same group in the periodic table 220 Exercises 222

Topics in *italics* are not included in W.B.H.S. Syllabi.

6. **SULPHUR AND ITS COMPOUNDS** ... ... 226—277

Natural sources of sulphur 226 Extraction of sulphur 226 Allotropic modification of sulphur 228 Properties of sulphur 230 Preparation of hydrogen sulphide in the laboratory 235 other methods of preparation of H_2S 236 Properties of hydrogen sulphide 237 The use of hydrogen sulphide as a reagent in the qualitative analysis of metallic salts 240 Preparation of sulphur dioxide 243 Properties of sulphur dioxide 244 Preparation of sulphur trioxide 252 Properties of SO_3 253 Preparation of sulphurous acid 256 Properties of sulphurous acid 256 Preparation of sulphuric acid 258 Large scale preparation of sulphuric acid by contact process 259 Properties of sulphuric acid 262 *Thiosulphuric acid and thiosulphates 270 Per disulphuric acid 271 Per monosulphuric acid 272* Some problems regarding the reactions of S and its compounds 273 Exercises 274

7. **HALOGENS AND THEIR HYDRACIDS** ... ... 278—337

Occurrence of fluorine 279 Preparation of fluorine 280 Properties of fluorine 283 Uses of fluorine 285 Preparation of chlorine 286 Manufacture of chlorine 289 Properties of chlorine 289 Test for chlorine 295 Uses of chlorine 295 Preparation of bromine 296 Properties of bromine 297 Preparation of iodine 300 Properties of iodine 302 Tests of iodine 304 Uses of iodine 305 Preparation of hydrogen fluoride 309 Properties of hydrofluoric acid 310 Tests of HF and fluorides 312 Uses of hydrogen fluoride 312 Preparation of hydrogen chloride 313 Properties of hydrogen chloride 315 Tests of hydrochloric acid and chlorides 318 Uses of hydrochloric acid 318 Preparation of hydrogen bromide 319 Properties of hydrogen bromide and hydrobromide acid 321 Test of hydrobromic acid and bromides 322 Uses of hydrobromic acid 322 Preparation of hydrogen iodide 323 Properties of hydrogen iodide 325 Tests of hydrogen iodide and iodides 326 Uses of hydrogen iodide 327 Some important oxycompounds of chlorine 331 Exercises 334

- **APPENDIX** 339
- **QUESTIONS** (H. S. & JT. Ent.) ... ... [i]

Topics in *italics* are not included in W.B.H.S. Syllabi.

INTRODUCTION

1. Introduction.

The fundamental activity of science is making careful observations. These observations may be of both qualitative and quantitative nature. They often involve controlled experiments. They are not merely collections of facts. These informations interpreted logically may lead to the evolution of science. Man ever since his existance, collected facts and interpreted them with reasons. Superstitions and obscure religious thinkings heading out with civilisation, darkened the power of reasoning to some extent. Study of natural phenomenon and its causes unearthed the shortcomings of the process of enquiry and thus came to being the logical reasoning process. Thus began the concept of science.

Science is nothing but a logical interpretation of nature. Different philosophers looked at the concept of science from different angles. Some considered science to be a tool of understanding and controlling nature in accordance with the developing needs of mankind, while others believed that science was a collective activity of mankind. According to Webstar (New international dictionary) '*science is a branch or department of systematic knowledge.*'

A more logical idea of science is that it is a branch of study concerned with observations and formulation of general laws chiefly by induction and hypothesis. Thus science is a descriptive knowledge of nature which is acquired through enquiries and thoughts, free from any prejudice.

The aims of science are :

(i) to attain truth through rational thinking after carefully experimenting the facts or data in the laboratory,

(ii) to develop the ability of concentrating on a problem and to find a solution through qualitative and quantitative approaches,

(iii) to utilise human/natural resources through the application of our five senses for the betterment of future generations,

(iv) to acquire and disseminate an overall knowledge of nature.

While investigating a problem, the first aim of a scientist should be to collect facts through experiments. If a large number of experiments give identical results, they can be summarised in a short statement. Such a statement is known as *law*. Hence **law** *is a concise statement summarising the results of a large number of separate experiments—all leading to the same conclusion.* In short, *law is the shortest statement of experimentally verified facts.*

It is essential to prove the enunciated law and it is done by suggesting a hypothesis. *A* **hypothesis** *is an idea or a collection of ideas on the basis of which the observed facts are explained and correlated.*

When the observed facts or natural laws are verified and accepted beyond doubt, they are restated in the form of a proper statement and this is then called a **theory**.

2. Chemistry and its branches.

Natural science is the perfect and systematic knowledge of different subjects of nature. Chemistry is an important and highly developed branch of natural science. The word 'Chemistry' has been derived from the Greek name *'Chemia'* apparently derived from the ancient name *'Chemi'* for Egypt where this branch of science was highly developed and widely practised at the beginning of the Christian era.

Chemistry is a branch of science which deals with the study of matter, its structure and composition, nature and transformation and the chemical changes brought upon it with the change of environment. The inter action of matter and energy is the primary object of studying chemistry.

As a result of constant researches the frontier of chemistry is expanding day by day and so for the convenience of study, chemistry has now been divided into several branches :

(i) **Inorganic Chemistry :** Except carbon and its compounds, the other 104 elements and the compounds that are formed by the mutual combination of these elements are studied under this branch of chemistry.

(ii) **Organic Chemistry :** Organic chemistry is the chemistry of carbon and its numerous compounds which are of vital importance in the biological world.

(iii) **Physical Chemistry :** This branch of chemistry deals with the laws or principles which govern chemical phenomenon. It helps to correlate and systematise the vast number of facts supplied by the organic and the inorganic chemistry.

(iv) **Analytical Chemistry :** This branch of chemistry deals with the qualitative detection and quantitative estimation of matter.

(v) **Bio Chemistry :** Bio chemistry deals with the study of chemical changes which are constantly going on in a living organism.

Besides the above-mentioned branches, modern chemistry has also other frontal organisations, e.g., *Geochemistry* (chemical study of minerals, stones in earth's crust), *Nuclear chemistry* (study of atomic nucleus), *Soil chemistry* (study of soil and fertilizer), *Quantum chemistry* (theoretical study of atomic particles) etc.

3. History of Chemistry.

Chemistry as an art was practised by mankind thousands and thousands years ago. The early civilisation of India, China, Egypt, Babylonia made positive contributions towards the early development of this science. The primitive people knew the extraction of iron from its ores, its casting, reformation of glass, use of colouring matter and the art of dyeing. The ancient philosophers also thought of the nature of matter, its constitution and the forces which affected the matter. The most fascinating idea of the atomic theory was conceived by the Indian philosopher **Kanad** who suggested that the ultimate particles of matter, called by him as *'Paramanu'* (atom), were finite.

The development of chemistry from the early age to the present day can be divided into the following three stages :

(i) *Period of alchemy :* (up to the 15th century).
(ii) *Iatro Chemistry :* (from the 16th century upto the middle of the 17th century).
(iii) *Scientific Chemistry.*

(i) **Period of alchemy :** From the first century A.D. some people of Egypt had an idea that any metal could be converted to gold by means of some 'agent' called 'Philosopher's stone'. This led to alchemy which is derived from the Arabic article *'al'* and the Greek name *'Chemiya'*. Alchemistry was an amalgamation of obscure religion, primitive superstitions and the rudimentary science. The exponents of this school of thoughts were **Roger Bacon, Basil Valentine** and Arabic school **Geiber.** According to them metals contained the primary element 'mercury' which was responsible for their metallic properties and sulphur was responsible for their combustibility and colour. In course of their attempt to discover the 'philosopher's stone' the alchemists developed many chemical processes, e.g., filtration, distillation, sublimation etc., which are used even today in our laboratory. At the beginning of the 15th century the practice of alchemy found its natural death.

(ii) **Iatro chemistry :** With the decline of alchemy there developed a new concept of using chemistry to discover *'elixir of life'* which could give perpetual youth. **Paracelsus** (1493 - 1541), who declared that the preparation of medicine should be the motto of philosophers and chemists, was the founder of this idea. **Libavius, Agricola, Lemary** etc., were famous during this period. Knowledge of chemical preparation of compounds made a shining advancement of chemistry in this period. In India **Nagarjuna, Charak, Susrut, Chakrapani** were some of the great exponents of medicinal chemistry. In spite of the failure to discover the *'elixir of life'* the Iatro-chemists isolated many chemical compounds from vegetable kingdom, earmarked many medicinal plants which are helpful even today.

(iii) **Scientific chemistry :** Renaissance in Europe in the 17th century gave a new impetus to the study of science from a new angle. **Robert Boyle** (1627—1691) was the founder of modern scientific chemistry. **Lavoisier** proved that air was not an element but a compound. **John Dalton** presented his famous atomic theory. **Avogadro** suggested the concept of molecule. **Cavendish** proved water to be a compound and not an element. Towards the middle of the last century atom was disintegrated by **William Crookes** which opened a new chapter in the development of science in general and chemistry in particular. A true picture of atomic structure was revealed due to the joint attempt of **Rutherford, Bhor, Millikan, Thomson,** etc. **Madam Curie** discovered radium, polonium which helped a lot to know much about the structure of atomic nucleus. **Seaborg** discovered the transuranic elements. Scientists were able to convert mass into an enormous amount of energy by splitting up the nucleus of an atom and as a result atom bomb and hydrogen bomb were created by **Otto Hahn, Strassmann** etc. The frontier of chemistry is thus expanding by leaps and bounds from the macro to the micro world.

4. Chemistry in India.

The use of copper and bronze and other evidences found in the relics of Mohenjodaro and Harappa go to prove that the chemical technology in ancient India made a tremendous progress. Medicinal chemistry made a phenomenal progress in ancient India. Preparation and use of drugs for the cure of dreadful diseases from medicinal plants were known to ancient India. The iron pillar in Delhi which was built around 300 A.D. proves that iron smelting had reached a high level of perfection in ancient India.

Some world famous research works were carried out in India in the 19th century which includes **Ronald Ross's** discovery of malaria parasites, **Robert Koch's** works on coma bacilli. In the first quarter of the present century **U.N Brahmachary** discovered urea-stibamine which eradicated black fever from Indian soil. The discovery of mercurous nitrite in 1898 by **Sir P. C. Roy** received a world wide attention. At present 8 chemical journals are published from India, some of which are internationally recognised. At present life-saving drugs are manufactured in India.

5. Matter.

Anything that occupies space, possesses mass and inertia is called matter. Matter can transfer motion and can neither be created nor be destroyed.

From chemical point of view *the matter which is made up of one kind of material is called a pure substance.* A pure substance is always homogeneous. On the basis of the internal structure, the pure substances are divided into two classes :—(i) *Element* and (ii) *Compound.*

(i) **Element** : *An element is a pure substance which cannot be split up by physical or chemical means into simpler and dissimilar substances.*

The molecules of an element consist of the same atoms. Thus hydrogen is an element because a molecule of hydrogen is composed of 2 atoms of hydrogen.

So far 105 elements are known to us. Of these 92 elements are natural and the remaining 13 are artificially synthesised in the laboratory. The *last reported* element is *Hanium* (Ha) of atomic number 105. The *lightest* element is *hydrogen* (At. No=1). There are 11 elements which are *gases at room temperature*—these are H_2, O_2, F_2, N_2, Cl_2, He, Ne, Ar, Kr, Xe and Rn. There are two elements which are liquid at room temperature e.g., *mercury* and *bromine*. The element *galium* (At. No = 31) is unique in nature as it melts at 30°C, yet it is not very volatile at red heat.

The elements can further be classified as (a) metal, (b) non metal, (c) metalloid.

(a) *Metal* : A metal is defined as an element which is solid (except mercury) at room temperture, can easily give up electrons. It has reducing property and low ionisation potential. Metals normally occupy the left side of the periodic table, and generally form electrovalent bonds e.g., Sodium (Na), Potassium (K), Magnesium (Mg), Iron (Fe), Gold (Au), Copper (Cu) etc.

(b) *Non metal* : A non-metal is defined as an element which is either gas or liquid at room temperature (except B, Si, C, I and S, which are solids), has a strong affinity for electrons. It has oxidising property, high electro-negativity and high ionisation potential. Non-metals normally occupy the right side of the periodic table and usually form the covalent bonds.

(c) *Metalloid* : The elements which exhibit more or less the properties of both metals and non metals, are called metalloids. e.g., Arsenic and Antimony.

The relative abundance of different elements in earth's crust is tabulated below :—

Elements	Percentage	Elements	Percentage
Oxygen	49·13	Potassium	2·35
Silicon	26·00	Magnesium	2·24
Aluminium	7·45	Hydrogen	1.00
Iron	4·20	Titanium	0·63
Calcium	3·25	Other trace elements	1.35
Sodium	2.40		

(ii) **Compound** : *A compound is a pure substance which is composed of two or more elements combined together in definite proportions by weight.*

The chemical combination of elements takes place through the union of atoms by valence forces. As a result of these forces, the combined elements are totally transferred into new domain having entirely different properties. Thus when electricity is passed through slightly acidified water, it decomposes into hydrogen and oxygen, the physical and chemical properties of which are quite different from that of water. Again it has been found that 1 part by weight of hydrogen combines with 8 parts by weight of oxygen in the presence of electric spark to produce 9 parts by weight of water. Thus, *water is a chemical compound.* Carbon di-oxide, sugar, sodium chloride, acids, bases and salts are examples of compound.

6. Mixture or mechanical mixture.

A mixture is the resulting substance obtained by mixing two or more elements or compounds or both in any proportions by weight without undergoing any chemical reaction between them.

Mixtures may be of different types. They may exist in solid, liquid or gaseous states. The different components in mixture can be separated from each other and the respective properties of the components in mixture are not changed. Depending on the physical state of the components there may be various types of mixtures. Thus air is a mixture of two gases, mainly oxygen and nitrogen. Brass is a mixture of copper and zinc ; milk is a mixture of protein, fat and water ; sugar solution is a mixture of sugar and water.

7. Physical and chemical changes.

Under the influence of various external conditions chemical substances may undergo two types of changes—(i) **Physical change** and (ii) **Chemical change.**

(i) **Physical change :** *A physical change is one which can alter some specific properties of a matter, like colour, texture, or state of aggregation but is incapable of bringing about any change in the composition of its molecules i.e., no new substance is produced as a result of this change.*

Magnetisation of iron, condensation of water vapour into liquid water and further into ice, are the examples of physical change, A platinum wire when held in a non-luminous flame becomes white hot and emits light. When it is removed from the flame its original state is restored again. Thus the platinum wire when heated in a flame suffers a physical change.

It should be borne in mind that in a physical change the weight of the original substance remains unchanged, it is temporary and the substance returns to its original form when the external agency of the change is withdrawn. In a physical change a thermal change may or may not occur.

(ii) **Chemical change :** *A chemical change is one which alters the characteristic properties of a matter by changing qualitatively the composition or the constitution of molecules.*

A chemical change is a permanent change and always produces a new chemical compound. A chemical change is always accompanied by a thermal change. When electric current is passed through water, it decomposes to give hydrogen and oxygen. The properties of H_2 and O_2 are entirely different from that of water. These two gases when mixed together cannot be reconverted to water. This is an example of a chemical change.

- **Distinction between physical change and chemical change.**

Physical change	Chemical change
(1) No new substance is formed by this change.	(1) Entirely new substance is produced by this change.
(2) Physical change is temporary—the changed substance can be easily reconverted to the original by removing the cause of change.	(2) This change is permanent,—cannot be reversed by removing the cause of change.
(3) This change may or may not be accompained by a thermal change.	(3) Chemical change is always accompanied by a thermal change.
(4) No change in the weight of the substance.	(4) Although the total weight of the reactants and the products remains the same, the individual reactants changes in weight.

8. Exothermic and Endothermic change.

When a matter undergoes a chemical change, it is always accompained by a thermal change i.e., a change in energy which manifests itself with the evolution or absorption of heat.

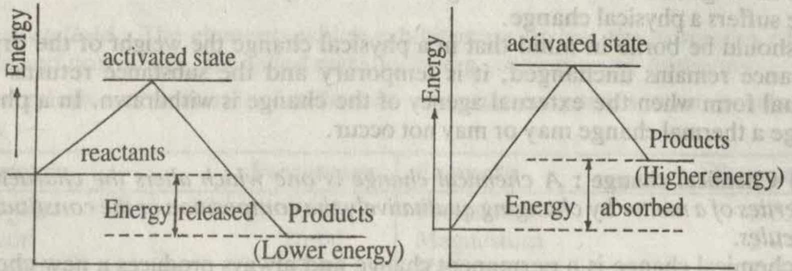
Exothermic reation : *Any chemical reation which is accompanied by the evolution of heat, is known as exothermic reaction.*

The compound which is formed as a result of an exothermic reaction is called an exothermic compound.

Thus during the burning of carbon in air or in the synthesis of ammonia from N_2 and H_2, heat is evolved. These are exothermic reactions and CO_2 and NH_3 are exothermic compounds.

$$C + O_2 = CO_2 + 97\ \text{k cal} \qquad N_2 + 3H_2 = 2NH_3 + 22.4\ \text{k cal.}$$

Since 97 k cal of heat are evolved in the formation of one mole of CO_2 from 1 gram atom of C and 1 mole of O_2, it is evident that 97 k cal of heat are evolved due to the release of energy from the reactants. Consequently CO_2 (product) contains less energy than the reactants i.e., in an exothermic reaction the *internal energy (enthalpy)* of the products will be less than those of the reactants.



Exothermic reaction

Endothermic reaction

Fig. 1

Endothermic reaction : *Any chemical reaction which is accompanied by the absorption of heat, is known as endothermic reaction.*

The compound which is formed as a result of endothermic reaction is called an endothermic compound.

The synthesis of carbon di-sulphide from carbon and sulphur, nitric oxide from nitrogen and oxygen are examples of endothermic compounds.

$$C + 2S = CS_2 - 28\text{ k cal}, \qquad N_2 + O_2 = 2NO - 43.2\text{ k cal}$$

Since 43.2 k cal of heat are absorbed during the formation of two moles of nitric oxide from 1 mole of N_2 and 1 mole of O_2, it is evident that 43.2 k cal of heat are absorbed which flow into the system from the surroundings. Consequently NO (product) contains more energy than the reactants, i.e., in an endothermic reaction the internal energy *(enthalpy)* of the products will be greater than those of the reactants.

As the exothermic compound contains less energy than its constituent elements it is more stable (less reactive) than endothermic compounds On the otherhand, an endothermic compound contains more energy than its constituent elements and so it is less stable i.e., more reactive and is easily decomposed.

- **Distinction between Mechanical Mixture and Chemical Compound.**

Mechanical mixture	Chemical compound
(1) A mechanical mixture results when two or more elements or compounds or both are mixed in any proportion by weight.	(1) In a chemical compound the ingredients are present in a fixed proportion by weight.
(2) In a mechanical mixture the ingradients may lose their physical properties but chemical properties of the individual ingredient are not at all changed.	(2) The chemical properties of the constituents are totally changed, and new properties are developed.
(3) The ingredients are found to lie side by side in a mechanical mixture.	(3) The ingredients chemically combine to form a new chemical compound.
(4) No chemical bond is found to be present among the ingredients of a mixture.	(4) The ingredients of a chemical compound are united by definite bonds and the structures of the reactants are completely changed.
(5) A mixture may be homogeneous or heterogeneous, e.g. an aqueous solution of NaCl is homogeneous while a mixture of sand and NaCl is heterogeneous.	(5) A chemical compound is always homogeneous.
(6) The ingredients of a mechanical mixture can be separated by easy mechanical means.	(6) The constituents of a chemical compound cannot be separated by mechanical means.
(7) During the preparation of a mechanical mixture thermal change may or may not take place. In case of preparation of some solutions thermal changes are observed.	(7) During the formation of a chemical compound, there is always a thermal change.
(8) A mechanical mixture has no fixed melting or boiling point. The m.p. and b.p. of a mixture vary with the change in the proportion of the ingredients.	(8) A chemical compound has a fixed melting point (in case of solid) and a, fixed boiling point (in case of liquid).

• EXERCISE •

1. What is science ? Define chemistry.

2. Trace the development of chemistry. Evaluate the contributions of Indian chemists to this development.

3. Define Matter. Name one metal, a metalloid and a non-metal. Name two metals which are liquid at room temperature.

4. Tabulate the differences between mechanical mixture and chemical compound. Give illustrations.

5. Which of the following is element, compound and mixture ?

Iodine, Mercury, Milk, Diamond, Brass, Sulphur, Gun powder, Smoke, Common salt, an aqueous solution of sugar, soda water.

6. Why is nitrogen called an element while carbon di-oxide a compound ?

7. State two elements which are present in the following materials : *(I.I.T. 1971)*

(a) Glass (b) Brass (c) Solder (d) Polythene.

8. Explain with illustrations exothermic and endothermic reactions.

9. “Although a solution has the same characteristics of a chemical compound yet it is a mixture. Explain the statement.

10. Iron fillings and sulphur powder are mixed together intimately. Do you observe any change ? Now the mixture is strongly heated. What changes will be observed ? What is the compound formed ?

1

STOICHIOMETRY

There are 92 naturally occurring elements mostly in combined form—a few in the free state. Chemical changes are rampant in nature i.e., elements combine to give compounds having varied combinations. On the other hand, these compounds decompose to give the elements which thus return back to the nature. In the laboratory various reactions are carried out to form new compounds from the natural ones. Initially these experiments were carried out qualitatively, but with the introduction of measuring equipments i.e., chemical balance, these experiments were advanced to the quantitative level. Credit goes to Lavoisier for the introduction of quantitative experimental chemistry in the late 18th century. The results obtained from these sets of experiments concluded that the chemical combinations take place according to some well defined chemical laws. These laws govern the mode of combination of different elements to form compounds. These laws are known as *the laws of chemical combinations* or *stoichiometric laws*. These are—

(i) *Law of conservation of mass* (Lavoisier, 1774)
(ii) *Law of constant* or *definite proportions* (Proust, 1799)
(iii) *Law of multiple proportions* (Dalton, 1803)
(iv) *Law of reciprocal* or *equivalent proportions* (Richter, 1799)
(v) *Law of gaseous volumes* (Gay Lussac, 1808)

The first four laws discuss the weight relationship between reactant(s) and product(s), while the fifth one deals with the combination of gases by volumes. All these laws have been proved experimentally and have theoretical interpretations.

1.1. Law of conservation of mass or law of indestructibility of matter.

This law was first proposed by **Lavoisier** in 1774. The law states that—

In a chemical change the total mass of the reactants is equal to the total mass of the products, or matter can neither be created not destroyed.

Example : (i) If *A* and *B* combine to form different products *C* and *D*, the total mass of *A* and *B* before the chemical reaction, is equal to the total mass of *C* and *D*.

i.e., *mass of A + mass of B = mass of C + mass of D*.

(ii) In the reaction $2H_2(g) + O_2(g) = 2H_2O(l)$ it is found that 4 parts by weight of hydrogen combine with 32 parts by weight of oxygen to form 36 parts by weight of water. The total mass of the reactants (4 + 32) g, is identical with the mass of the product (36 g). This is true for all chemical reactions.

- **In some changes (chemical as well as physical) some apparent anomalies are observed and it appears that the law of conservation of mass is not true.**

(i) Some chemical and physical changes in which the mass is apparently lost :

(a) A burning candle slowly decreases its mass and finally nothing is left behind. Similarly spirit, petrol or kerosine on combustion completely disappear and no visible residue is left behind.

(b) A piece of charcoal on ignition continues to burn and finally leaves behind only ash as residue. The weight of this ash is found to be much less than that of the original piece of charcoal.

(c) A piece of camphor on being left exposed to atmosphere, diminishes in size and the loss of its weight is noticed.

In all the above changes, the mass appears to be lost and this may lead to an idea that matter has been destroyed in the above cases.

Explanation : A close scrutiny of the above changes shows that the apparent decrease of mass during a chemical reaction is nothing but transformation of matter—no matter is destroyed during the changes.

(a) Candle, petrol or kerosine are nothing but the compounds of carbon and hydrogen. On combustion they combine with O_2 of atmosphere and form CO_2 and water vapour and escape in the air. Hence is the observation of the loss in mass during combustion. But if the quantitative measurements are made, it will be observed that the total mass of the candle or petrol or kerosine and the oxygen consumed for their combustion is the same as the total mass of CO_2 and H_2O produced i.e.,

the mass of candle + mass of O_2 consumed = the mass of CO_2 + mass of water vapour formed.

Thus it is proved that in each of the above chemical changes, the total mass of the reactants is equal to the total mass of the products.

(b) When a piece of comphor is left exposed to the atmosphere a decrease in the mass of camphor is observed. But this loss in mass does not contradict the law. Camphor spontaneously sublimes at room temperature. Camphor loses in mass as its vapour escapes into the atmosphere as soon as it is formed. If the weight of the vapour and the weight of the residual camphor are taken, it will be found that the total weight of the vapour and the residual camphor is equal to the weight of the piece of camphor originally taken. It is nothing but a simple transformation of matter.

(ii) Some chemical changes in which the mass is apparently gained :

(a) A piece of magnesium on heating strongly in oxygen, continues to burn with a dazzling glow and finally leaves a white residue, the mass of which is found to be greater than that of the original magnesium. This shows that magnesium increases in weight on burning.

(b) A piece of iron nail of known weight is taken and is left exposed to moist air. After some days it is found that a brown coating of rust develops on the surface of the iron nail. The weight of the rusted iron nail is found to be heavier than that of the original iron nail. From these observations,one may conclude that new matter has been created in this chemical change, contradicting the law of conservation of mass.

Explanation : (a) When a piece of magnesium is burnt in oxygen, it combines with a definite weight of oxygen and is converted to magnesium oxide which is left as white residue. $2Mg + O_2 = 2MgO$. The residue is found to be heavier than the original magnesium as O_2 has combined with magnesium during the combustion. Now if the weight of the magnesium oxide produced is taken, it will be found to be equal to the total weights of magnesium initially taken and the oxygen consumed for its burning.

i.e., ***Wt. of Mg + Wt. of O_2 consumed = Wt. of MgO produced.***

(b) A brown coating of rust formed on the iron nail when it is left exposed to moist air is due to the formation of hydrated ferric oxide. So the iron nail is found to gain in weight. The weight of iron nail increases as some amount of O_2 and moisture of air are added to iron during this chemical change. Consequently the weight of rusted iron will be the same as the sum of the weights of the iron nail, the moisture and O_2 added.

Thus, in all chemical changes only transformation of matter takes place but the matter is neither created, nor destroyed. Thus the law of conservation of mass holds good in all types of changes.

- **Experimental proof of the law of conservation of mass.**

1. Lavoisier's experiment :

It was Lavoisier who first proved the law of conservation of mass experimentally. He took some tin foils in a glass retort and sealed its mouth carefully. The retort was then weighed with its contents. It was then heated for a long period when a part of the metallic tin combined with the oxygen of air inside the retort to form tin oxide. The retort was then cooled and weighed. The first and the second weight were found to be identical. Thus it proved that although metallic tin was converted to tin oxide, there was neither increase nor decrease of the total weight. In other words, matter underwent transformation but no creation or destruction of matter occurred.

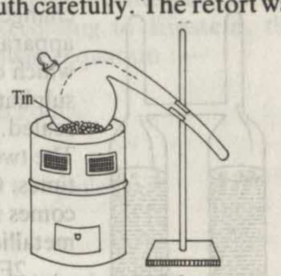


Fig. 1·1 : Lavoisier's experiment

2. Partington's candle light experiment :

A hard glass tube, open at both ends is taken, the diameter of which is 5 cm and the length 20 cm. Near the upper end, the tube is fitted with a copper wire gauze with layers of lime and soda lime [$NaOH + Ca(OH)_2$] on it. The upper end of the tube is now closed with a rubber cork. The lower end of the glass tube is closed with a perforated cork on which is mounted a small candle. The perforation in the cork is made to provide ventilation to candle for its smooth burning. The entire unit thus prepared is suspended from the left arm of a chemical balance. The unit containing the candle is weighed accurately. The weights on the pan of the right arm are not removed. Now, the perforated cork is opened and the candle is lighted and quickly put back to its initial position. As the candle burns, a partial vacuum is produced inside the tube and air is drawn inside the tube through the perforations of the cork and thus the candle continues to burn inside the glass tube.

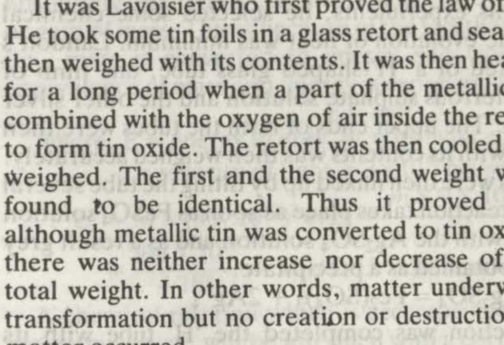


Fig. 1·2 : Candle light experiment

Observation : When the candle is burnt out completely, it is observed that instead of decrease in the weight of the apparatus, the left arm of the balance is tilled towards the left. It thus records the increase in weight of the glass tube.

Conclusion : From this experiment it can be concluded that the mass of the candle is not destroyed even when completely burnt out. On the contrary it is not true that this increase in weight means the creation of some new matters.

Explanation : A candle is a compound of hydrogen and carbon. During its burning, the carbon and hydrogen of the candle combine with the oxygen of air to form carbon di-oxide and water vapour respectively. The gaseous products thus formed cannot escape as they are absorbed by lime and soda lime kept on the copper wire gauze. The weight of the glass tube increases according to the weight of the oxygen consumed for the complete combustion of the candle. If the weight of the oxygen consumed for the complete combustion of the candle were known, then it would be seen that :—

The wt. of the candle + the wt. of O_2 *consumed = the wt. of* CO_2 *+ the wt. of* H_2O.

3. Landolt's Experiment :

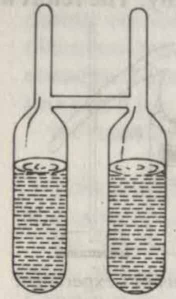


Fig. 1·3 : Landolt's experiment

By far the best experiment for establishing the validity of the law of conservation of mass comes from Landolt. For his experiments, he selected some chemical changes where the evolution of heat was minimum. Landolt's apparatus consisted of a 'H'-shaped glass tube, one limb of which contained ferrous sulphate solution and the other silver sulphate solution. The upper ends of both the tubes were then sealed. The tube with its contents was then weighed accurately. The two solutions were then mixed up by tilting the tube several times. Chemical reaction takes place as soon as $FeSO_4$ solution comes in contact with the Ag_2SO_4 solution and as a result grey metallic silver is obtained as a precipitate.

$$2FeSO_4 + Ag_2SO_4 = Fe_2(SO_4)_3 + 2Ag \downarrow$$

When the reaction was completed the 'H' tube with its contents was weighed again. It was found that the first and the second weight were identical. Thus it is proved that there has been no creation or destruction of matter — only a simple transformation of matter has taken place.

[Landolt carried out this experiment with 15 pairs of solutions and found that the experimental error was only 3 parts in 35×10^6. Manley (1912) carried out this experiment with greater accuracy by using solutions of $BaCl_2$ and Na_2SO_4]

This experiment can be carried out in the laboratory. Solutions of lead nitrate and potassium iodide are taken in two different test tubes. These two test tubes are taken in a conical flask and the mouth of the flask is closed with a rubber cork. The flask with its contents is then weighed accurately. Now the two solutions are mixed up by tilting the conical flask. As soon as the two solutions come in contact with each other reaction takes place with the formation of a yellow precipitate of lead iodide. After the completion of the reaction the flask is reweighed . It will be observed that the weight of the conical flask with its contents remains exactly the same.

$$Pb(NO_3)_2 + 2KI = PbI_2 \downarrow + 2KNO_3$$

4. Rusting of Iron :

Some shining iron nails are taken in a hard glass test tube and are kept immersed partially in water. The tube is then tightly corked to make it air tight. The closed tube with its contents is weighed accurately in a chemical balance and allowed to remain in that condition for a week. After that it is observed that the shining iron nails are covered with brown layer of rust. The tube with its contents is reweighed. It is found that the weight of the tube with its contents remains exactly the same as before, though there has been a chemical change due to the formation of rust.

Rust is the hydrated ferric oxide which forms as a result of the chemical combination of iron with the moist air inside the tube. The weight of the iron nails increases during their rusting as O_2 and H_2O combine with them to form the rust. Since the loss in weight due to O_2 and water vapour present inside the tube is responsible for the gain in weight due to the formation of rust, there is no change in the initial and the final weight i.e., the total mass before and after the reaction remains the same.

- **The law of conservation of mass in the light of interconversion of mass and energy—the law of conservation of mass is not absolutely true.**

In establishing the truth of the law of conservation of mass by Landolt or Manley, no reaction was investigated which involved the evolution of large amount of heat. According to modern theory of radiations, the law of conservation of mass is not absolutely true. Many chemical changes are practically accompanied by minute loss or gain of mass. This is because of the fact that mass and energy are interconvertible i.e., mass is converted to energy and vice versa. According to Einstein, the equivalence of mass and energy is expressed by the following equation :—

$$E = mc^2 \qquad \therefore\ m = E/c^2$$

where, E = energy in ergs, m = its mass equivalent in grams.

c = velocity of light = 3×10^{10} cm/sec.

$$\therefore\ E = m \times (3 \times 10^{10})^2 \text{ ergs} = \frac{m \times 9 \times 10^{20}}{10^7} = 9m \times 10^{13} \text{ joules}$$

$$= \frac{9m \times 10^{13}}{4{\cdot}184} = m \times 2{\cdot}15 \times 10^{13} \text{ calories.}$$

A chemical reaction which is accompained by an emission of energy, usually in the form of heat, will be attended with a corresponding loss of mass $m = E/c^2$. But since c is very large, the loss of mass will be insignificantly small. It has been estimated that energy liberated in any ordinary chemical reaction requires a conversion of about 1×10^{-11}gm of matter into energy. On burning 3·75 tons of phosphorus, a loss of 1 mg mass is recorded. Thus, for ordinary chemical reactions such microscopic conversions of mass into energy are neglected. The law of conservation of mass in its simple form, holds good for ordinary chemical reactions.

However, in *nuclear reactions* i.e., *nuclear fission and fusion,* an enormous amount of energy is liberated by the conversion of an extremely small amount of matter. Like the conservation of mass, *energy can neither be created nor destroyed. One form of energy can be transformed to other, without any gain or loss in the total amount of energy.* Thus *the total energy in the universe is constant.* This is known as the *law of conservation of energy.*

If matter is regarded as a form of energy (*matter is a bottled energy—as postulated by Jeans*) it can be stated that matter plus energy remain constant in any isolated system. The law of conservation of mass and the law of conservation of energy are now combined into a single law which is expressed as :—

The total quantity of matter and energy in an isolated system is always constant. In other words, *in any reaction, the total amount of mass and energy remains constant.*

1.2. The law of definite or constant proportions.

This law was first proposed by Proust in 1797 and subsequently verified by Stas in 1865. The law states that :

The same compound always contains the same elements combined together in the same fixed proportions by weight and its composition is independent of the methods by which it is prepared

Explanation : The same compound may be prepared in different ways and may be obtained from different sources, but the composition of the particular compound will be identical, no matter how and from what source it is prepared.

Let a particular compound is composed of two elements *M* and *N*, then according to the law of definite proportions whatever may be the source of the compound, it will always contain the elements *M* and *N* only. Now let the compound be prepared by two diffferent ways. In the first way let '*x*' g of *M* combine with '*y*' g of *N* and in the second method '*a*' g of *M* combine with '*b*' g of *N*. Then the law proposes—

$\frac{x}{y} = \frac{a}{b}$, i.e., the ratio of the weights of *M* and *N* remains constant.

Examples : The compound magnesium oxide may be prepared.

(i) by heating magnesium carbonate strongly,

$$MgCO_3 = MgO + CO_2 \uparrow$$

(ii) by heating magnesium hydroxide strongly,

$$Mg(OH)_2 = MgO + H_2O \uparrow$$

(iii) by heating magnesium nitrate strongly,

$$2Mg(NO_3)_2 = 2MgO + 4NO_2 \uparrow + O_2 \uparrow$$

Analysis of magnesium oxide thus prepared by different methods and from different sources shows that it contains the elements magnesium and oxygen only and the ratio by weight of magnesium to oxygen is always fixed, i.e., 3:2. This illustrates the law of definite proportions.

It has been found that every matter—solid, liquid or gas, has a fixed composition.

- **Experimental verification of the law of definite proportions.**

The compound cupric oxide is prepared from different sources by three different methods, by heating separately *Copper nitrate, Copper carbonate* and *Copper hydroxide*. The three samples of Cupric oxide thus obtained are labelled as Sample No. 1, Sample No. 2 and Sample No. 3 respectively.

$$2Cu(NO_3)_2 \xrightarrow[\Delta]{} \underset{\text{(Sample 1)}}{2CuO} + 4NO_2 \uparrow + O_2 \uparrow$$

$$CuCO_3 \xrightarrow[\Delta]{} \underset{\text{(Sample 2)}}{CuO} + CO_2 \uparrow$$

$$Cu(OH)_2 \xrightarrow[\Delta]{} \underset{\text{(Sample 3)}}{CuO} + H_2O \uparrow$$

A clean and dry porcelain boat is weighed and then a small amount of sample 1 cupric oxide is taken in the boat and weighed again. The boat with its content is then introduced into a hard glass combustion tube kept in horizontal position. The two ends of the combustion tube are closed with corks fitted with an inlet tube and an exit tube. Pure and dry hydrogen is passed through the inlet tube and the boat is heated strongly. The black cupric oxide is reduced by hydrogen to red metallic copper. Water formed as a product of the reaction passes out through the exit tube.

$$CuO + H_2 = Cu + H_2O \uparrow$$

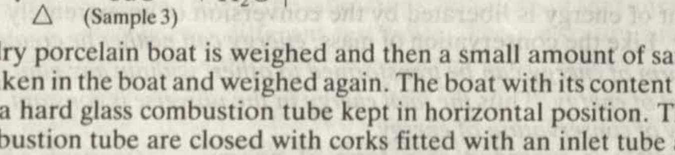


Fig 1.4 :

After the completion of the reaction, heating is stopped but the flow of hydrogen is continued till the combustion tube is cooled to room temperature. The boat with its contents is taken out and weighed accurately. The process of heating, cooling and weighing is repeated till the final weight is found to be constant.

Calculations : Let the wt. of the porcelain boat = m g

the wt. of procelain boat + CuO = m_1 g

the wt. of procelain boat + Cu = m_2 g

$\therefore$ the wt. of CuO = $(m_1 - m)$ g

the wt. of Cu = $(m_2 - m)$ g

$\therefore$ the wt. of oxygen in CuO = $(m_1 - m) - (m_2 - m)$ g $= (m_1 - m_2)$ g

Hence the percentage of Cu in CuO = $\dfrac{(m_2 - m) \times 100}{(m_1 - m)}$

the percentage of O_2 in CuO = $\dfrac{(m_1 - m_2) \times 100}{m_1 - m}$

The same experiment is repeated with the sample number 2 and 3 of pure cupric oxide. It is observed that within the limits of experimental error, the weight ratio of copper and oxygen in all the samples are the same. Thus the law of definite proportions is experimentally proved.

- **The converse of the law of constant proportions is not always true.**

The law of definite proportions characterises a definite compound but the law fails in some cases. The converse of the law of definite proportions states that, '*The elements combined in a definite proportion by weight will always produce the same compound.*' But it is not applicable in case of organic and inorganic isomers. The compounds having the same chemical composition but different chemical properties are called **isomers.**

Thus (i) *Ethyl alcohol* and *dimethyl ether* are found to contain the same elements—carbon, hydrogen and oxygen which are combined in the same weight ratios.

In ethyl alcohol (C_2H_5—OH) C : H : O = 12 : 3 : 8

In dimethyl ether (CH_3—O—CH_3) C : H : O = 12 : 3 : 8

But these two are entirely different compounds having different properties.

(ii) *Urea* [$CO(NH_2)_2$] and *ammonium cyanate* (NH_4CNO) are found to contain the same elements having the same weight ratios, but they are chemically different.

(iii) Two or more molecules of the same compound combine with one another to form an entirely different molecule. This type of intermolecular combination of the same compound is known as **polymerisation.** When acetylene gas is passed through a copper tube heated to 500°C, three molecules of acetylene combine together to form benzene molecule. Thus both acetylene (C_2H_2) and benzene (C_6H_6) have the weight ratio of C : H = 12 : 1. But acetylene is a gas and benzene is a liquid at ordinary temperature. Thus the converse of the law of constant proportions is not always true.

- **Law of constant proportions fails in some cases.**

(i) Sometimes union of elements may give rise to more than one compound. It happens in the case of elements having variable valency. Thus copper and chlorine on combination may give cuprous chloride (CuCl) and cupric chloride ($CuCl_2$), tin and oxygen combine to form SnO and SnO_2. The law of definite proportions is valid only when we consider one compound of each set, but the law becomes invalid when both the compounds of the same set are considered.

(ii) After the discovery of isotopes, it is found that the law is not applicable everywhere. It is now known that almost all elements consist of a mixture of isotopes. Thus hydrogen has 3 istopes of mass number 1 (Hydrogen), 2 (Deuterium) and 3 (Tritium). Now water from different sources having different isotopic compositions will automatically differ in weight ratio of hydrogen and oxygen. So any compound formed by the union of a particular isotopic species of elements, will register a difference in weight ratio of the constituent elements from that produced by the union of another isotopic species of the same element.

Due to the existence of isotopes it is essential to modify the statement of the law. The modified statement of the law of constant proportions can be expressed as—*A given compound always contains the same isotopes or a mixture of isotopes of the constituent elements combined in the same fixed proportions by weight.*

1.3. Law of multiple proportions.

The law states that—*when two elements combine to form two or more compounds, the different weights of one of the elements, which combine with a fixed weight of the other element, bear a simple ratio of whole numbers to one another.*

Exaplantion : According to this law, if two elements *X* and *Y* combine to form different compounds, say X_2Y, XY, XY_2 etc., then if say in XY, 10 g of *X* combine with 25 g of *Y*, then in the other compounds namely X_2Y, and XY_2, the weight of *X* combining with 25 g of *Y*, will always be some simple multiple of 10 i.e., 5, 10, 20 - - -g. Thus the ratio of *X* which combines with a fixed weight of *Y* is 5 : 10 : 20. i.e., 1 : 2 : 4. This is a simple ratio.

Examples : 1. Carbon and hydrogen combine to form series of hydrocarbons namely methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2) etc. On analysis we find that :

In Methane :—
12 parts by weight of carbon combine with 4 parts by weight of hydrogen.
In Ethane :—
24 parts by weight of carbon combine with 6 parts by weight of hydrogen.
In Ethylene :—
24 parts by weight of carbon combine with 4 parts by weight of hydrogen.
In Acetylene :—
24 parts by weight of carbon combine with 2 parts by weight of hydrogen.

Hence the different weights of hydrogen which combine with a fixed weight of carbon, i.e., 12 parts of carbon, are 4 : 3 : 2 : 1. This is a simple ratio.

Compound	**Weights of**		**Fixed weight of carbon**	**Weights of H_2 which combine with a fixed wt. of carbon**	**Ratio of the weights of hydrogen**
	Carbon	**Hydrogen**			
Methane (CH_4)	12	4	12	4	4 : 3 : 2 : 1 this is a simple ratio
Ethane (C_2H_6)	24	6	12	3	
Ethelene (C_2H_4)	24	4	12	2	
Acetylene (C_2H_2)	24	2	12	1	

2. Nitrogen, on combination with oxygen produces five different oxides. The weights of oxygen which combine with a fixed weight (14 parts) of nitrogen are tabulated below :—

Oxides of Nitrogen	**Weights of**		**Fixed weight of nitrogen**	**Weights of O_2 which combine with a fixed wt. of nitrogen**	**Ratio of the weights of oxygen**
	Nitrogen	**Oxygen**			
Nitrous oxide (N_2O)	28	16	14	8	8 : 16 : 24 : 32 : 40 = 1 : 2 : 3 : 4 : 5 i.e., a simple ratio
Nitric oxide (NO)	14	16	14	16	
Dinitrogen Trioxide (N_2O_3)	28	48	14	24	
Nitrogen dioxide (NO_2)	14	32	14	32	
Nitrogen pentoxide (N_2O_5)	28	80	14	40	

3. Copper reacts with chlorine to form cuprous chloride (Cu_2Cl_2) and cupric chloride ($CuCl_2$). The weights of chlorine which combine with a fixed weight of copper, i.e., 63·5 parts will be found to be 35·5 : 71 or 1 : 2 i.e., a simple ratio.

Compound	Weight of		Fixed weight of copper	Weights of Cl_2 which combine with the fixed wt of copper	Ratio of the weights of chlorine
	Copper	Chlorine			
Cuprous chloride	127	71	63·5	35·5	35·5 : 71 = 1 : 2 This is a sample ratio
Cupric chloride	63·5	71	63·5	71	

• Experimental verification of the law of multiple proportion :

Initially two dry procelain boats are weighed in a chemical balance. Some pure CuO and Cu_2O are taken in the boat No. I and II respectively. The boats are then carefully reweighed. The two boats with CuO and Cu_2O are placed side by side in a combustion tube as shown in the diagram (Fig. 1.5) and strongly heated. A stream of pure and dry hydrogen gas is passed through the tube. The oxides of copper are reduced to metallic copper by hydrogen.

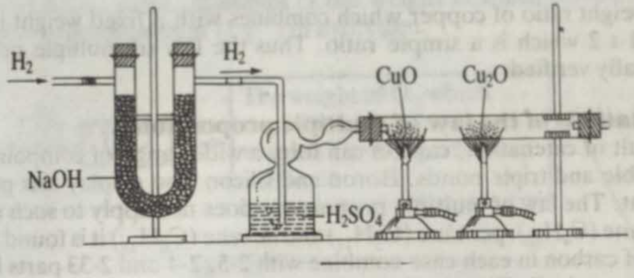


Fig. 1.5 : Verification of the Law of multiple proportions.

$$CuO + H_2 = Cu + H_2O \qquad\qquad Cu_2O + H_2 = 2Cu + H_2O$$

When the reduction is complete, the porcelain boats are taken out, cooled in a desiccator and carefully weighed again in a chemical balance. The processes of heating the boats in hydrogen, cooling in desiccator and weighing are repeated till the final weight in each case becomes constant.

Calculations :

(A) *With CuO in boat I :*

Weight of procelain boat = w g

Weight of porcelain boat + CuO = w_1 g

Weight of CuO = $(w_1 - w)$ g

Weight of porcelain boat + copper = w_2 g

Weights of copper = $(w_2 - w)$ g

Weights of oxygen = $(w_1 - w - w_2 + w)$ g $= (w_1 - w_2)$ g

Thus $(w_1 - w_2)$ g of O_2 combines with $(w_2 - w)$ g of copper to produce $(w_1 - w)$ g of CuO.

$\therefore$ 1 g of O_2 combines with $\frac{w_2 - w}{w_1 - w_2}$ g of copper = Let it be x g of copper.

(B) *With Cu_2O in boat II :*
Weight of porcelain boat = m g
Weight of boat + Cu_2O = m_1 g
Weight of boat + copper = m_2 g
hence, weight of Cu_2O = (m_1-m) g
Weight of copper = (m_2-m) g
and weight of oxygen = (m_1-m-m_2+m) g
= (m_1-m_2) g .

Thus (m_1-m_2) g oxygen combines with (m_2-m) g of copper to form (m_1-m) g of Cu_2O.

$\therefore$ 1 g of O_2 combines with $\dfrac{m_2-m}{m_1-m_2}$ g of copper = Let it be y g of copper.

In the above two results the weight of oxygen is fixed, and the weights of Cu are x g and y g respectively. In an actual experiment $\dfrac{x}{y} = \dfrac{1}{2}$

or, the weight ratio of copper which combines with a fixed weight i.e., 1 g of oxygen = 1 : 2 which is a simple ratio. Thus the law of multiple proportions is experimentally verified.

- **Limitations of the law of multiple proportions.**

As a result of catenation, carbon can form a wide range of compounds through single, double and triple bonds. Boron and silicon also display this property to a lesser extent. The law of multiple proportions does not apply to such compounds, e.g., in butane (C_4H_{10}), pentane (C_5H_{12}) and hexane (C_6H_{14}) it is found that 12 parts by weight of carbon in each case combine with 2·5, 2·4 and 2·33 parts by weight of hydrogen respectively. The weight ratio of hydrogen 2·5 : 2·4 : 2·33 is not definitely a simple ratio. Unless the meaning of the term "simple ratio" is severely strained, this law can never be applied to these cases.

Furthermore slight variation in the results will be observed if the isotopic constitution of the atom of the combining elements differ.

1.4. The Law of Reciprocal or Equivalent Proportions.

The chemical union between two elements leading to the formation of *one* pure compound was dealt with the law of definite proportions. The law of multiple proportions deals with the chemical union between two elements leading to the formation of more than one compound. The law of reciprocal proportions further extends the picture by dealing with chemical combination among more than two elements. The law was proposed by **Richter** in 1792. The law states—

The weights of two or more different elements which separately combine with a fixed weight of another element, are either the same as, or simple multiples or submultiples of the weights of these different elements when they combine among themselves.

Explanation : Let z g of an element C combine with x g of another element A to form a compound AC. Again z g of C combine with y g of another element B to form BC. Now if A and B combine together to form a compound, then according to the law of reciprocal proportions, the ratio by weight in which they would combine together will either be $x : y$ or some simple multiples or submultiples of x and y i.e., $mx : ny$, where m and n are simple whole numbers.

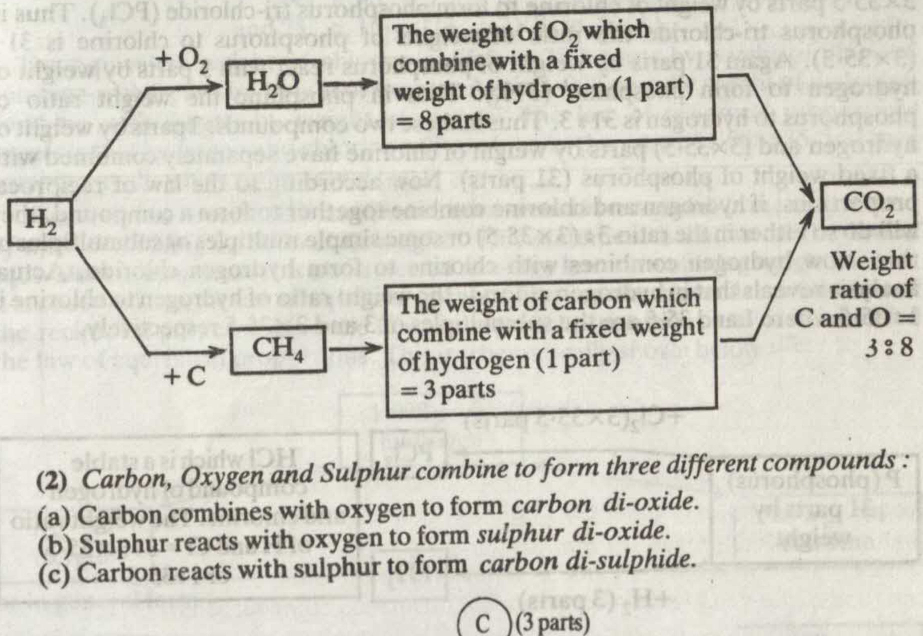
Examples :

(1) Hydrogen combines with carbon and oxygen separately to form methane and water respectively. Chemical analysis shows that in methane 12 g of carbon combines with 4 g of hydrogen. Hence in methane the weight ratio of carbon to hydrogen is 12 : 4 or 3 : 1. Again in water the weight ratio of oxygen to hydrogen is 8 : 1. Thus it is found that in the two compounds 3 parts by weight of carbon and 8 parts by weight of oxygen have separately combined with 1 part by weight of hydrogen.

Now according to the law of reciprocal proportions, if carbon and oxygen combine together, they would do so (i) either in the ratio 3 : 8, or (ii) in its simple multiples or submultiples. Now carbon reacts with oxygen to form carbon di-oxide (CO_2) and carbon monoxide (CO).

In carbon di-oxide (CO_2) the weight ratio of carbon to oxygen is 12 : 32 or 3 : 8 which is same as directed by the law.

In CO, the weight ratio of carbon to oxygen is 12 : 16 or 6 : 8 or (2 × 3) : 8. Now 6 is a multiple of 3, i.e., some, multiples of the weight in which carbon and oxygen combine with a constant weight (1 g) of hydrogen.



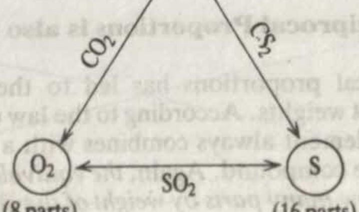
The weight of O_2 which combine with a fixed weight of hydrogen (1 part) = 8 parts

The weight of carbon which combine with a fixed weight of hydrogen (1 part) = 3 parts

Weight ratio of C and O = 3 : 8

(2) *Carbon, Oxygen and Sulphur combine to form three different compounds :*

(a) Carbon combines with oxygen to form *carbon di-oxide*.
(b) Sulphur reacts with oxygen to form *sulphur di-oxide*.
(c) Carbon reacts with sulphur to form *carbon di-sulphide*.



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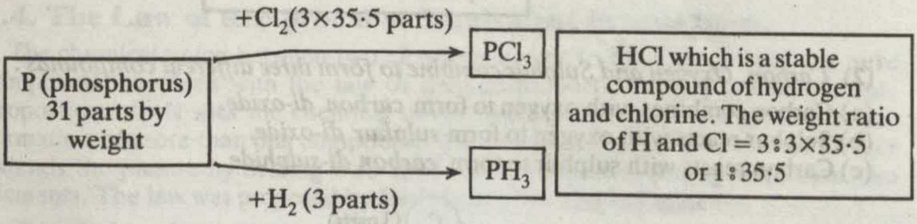
The following table shows the application of the law of reciprocal proportions in different compounds formed by the above 3 elements.

Fixed weight of Element	Different compounds of the element	Weight ratio of the element	Weight ratio of the elements in the possible compounds.
Carbon = 3 parts	(1) CO_2 (2) CS_2	C : O = 3 : 8 ↓ C : S = 3 : 16	S : O = 16 : 8. In SO_2 the weight ratio of S and O is found to be = 16 : 16. This can be written as S : O = 16 : (8×2). Again 2 is a whole number or 16 is a multiple of 8.
Oxygen = 8 parts	(1) CO_2 (2) SO_2	C : O = 3 : 8 ↓ S : O = 8 : 8	C : S = 3 : 8. In CS_2 the weight ratio of C and S is found to be = 3 : 16 or 3 : (8×2). Again 2 is a whole number or 16 is a multiple of 8.
Sulphur = 16 parts	(1) CS_2 (2) SO_2	C : S = 3 : 16 ↓ O : S = 16 : 16	C : O = 3 : 16. In CO_2, a compound of carbon and oxygen shows that the ratio of the weights of C and O is 6 : 16 or (3×2) : 16. Again 2 is a whole number or 6 is a multiple of 3

(3) Chemical analysis reveals that 31 parts by weight of phosphorus combine with 3×35·5 parts by weight of chlorine to form phosphorus tri-chloride (PCl_3). Thus in phosphorus tri-chloride the ratio of weights of phosphorus to chlorine is 31 : (3×35·5). Again 31 parts by weight of phosphorus react with 3 parts by weight of hydrogen to form phosphine (PH_3). Thus in phosphine the weight ratio of phosphorus to hydrogen is 31 : 3. Thus in these two compounds, 3 parts by weight of hydrogen and (3×35·5) parts by weight of chlorine have separately combined with a fixed weight of phosphorus (31 parts). Now according to the law of reciprocal proportions, if hydrogen and chlorine combine together to form a compound, they will do so either in the ratio 3 : (3×35·5) or some simple multiples or submultiples of this. Now hydrogen combines with chlorine to form hydrogen chloride. Actual analysis reveals that in hydrogen chloride the weight ratio of hydrogen to chlorine is 1 : 35·5 where 1 and 35·5 are the submultiples of 3 and 3×35·5 respectively.


+Cl₂(3×35·5 parts)
P (phosphorus) 31 parts by weight
PCl₃
HCl which is a stable compound of hydrogen and chlorine. The weight ratio of H and Cl = 3 : 3×35·5 or 1 : 35·5
PH₃
+H₂ (3 parts)

• The Law of Reciprocal Proportions is also called the Law of Equivalent Proportions.

The law of reciprocal proportions has led to the important conception of combining or equivalent weights. According to the law of reciprocal proportions, a definite weight of an element always combines with a definite weight of another element to form a stable compound. Again, *the equivalent weight of an element is a number which shows how many parts by weight of the element in question combines with or replaces from a compound 8 parts by weight of oxygen.*

Now 3 parts by weight of carbon combine with 8 parts by weight of oxygen to form CO_2. Again 8 parts by weight of O_2 combine with 23 parts by weight of sodium and 20 parts by weight of calcium to form Na_2O and CaO respectively. Furthermore, 1·008 parts by weight of hydrogen react with 8 parts by weight of oxygen to form H_2O. Hence by definition the equivalent weights of carbon, sodium, calcium and hydrogen are 3, 23, 20 and 1·008 respectively. Now when these elements combine among themselves they will do so either in the ratio of their equivalent weights or some multiples or submultiples of them.

Thus, sodium and hydrogen combine to form sodium hydride according to the following equation.

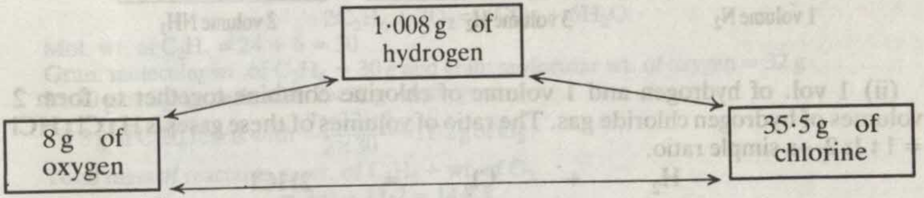
$$\underset{2\times 23\text{ g}}{2Na} + \underset{2\times 1{\cdot}008\text{ g}}{H_2} = 2NaH$$

The weight ratio of sodium to hydrogen is (2×23) : (2×1·008) or 23 : 1·008. The last two figures are the equivalent weights of sodium and hydrogen respectively. Similarly in calcium hydride (CaH_2), the weight ratio of Ca to H is 20 : 1·008. Again sodium and oxygen combine to form sodium monoxide (Na_2O) and sodium peroxide (Na_2O_2). The weight ratio of

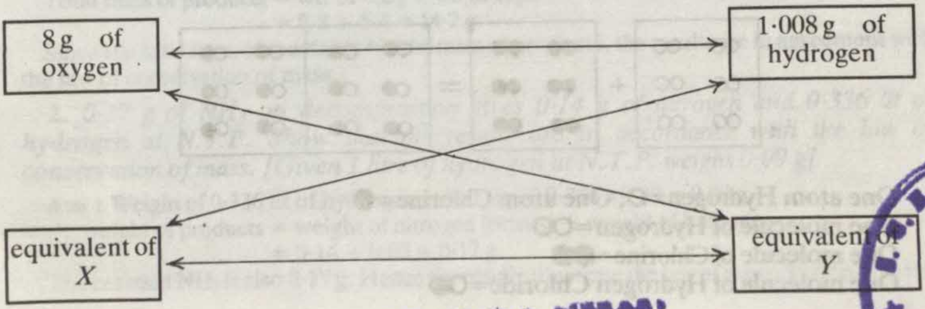
$$\begin{aligned} &Na : O = 23 : 8 \text{ in } Na_2O \\ \text{and } &23 : 16 \text{ or } 23 : 2\times 8 \text{ in } Na_2O_2 \end{aligned}$$

The equivalent weight of chlorine is 35·5 as 35·5 parts by weight of chlorine combine with 8 parts by weight of oxygen. Again 1·008 parts by weight of hydrogen combine with 8 parts by weight of oxygen. The law of reciprocal proportions suggests that hydrogen and chlorine will combine in the ratio of 1·008 : 35·5, if they combine at all, which is the actual fact.

Thus it can be concluded that *elements always combine together in the simple ratio of their combining or equivalent weights.* This statement is known as the **law of equivalent proportions.** It is also referred to as the **law of combining weights.** Thus, it is observed that the law of equivalent proportions is a direct corollary of the law of the reciprocal proportions or the law of reciprocal proportions may also be called the law of equivalent proportions. This is schematically shown below :—



or in general form :—



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- **Limitation of the law of reciprocal proportions :**

Just like the law of the multiple proportion, the results obtained from this law register a slight variation which is attributed to the difference in the isotopic constitution of the atoms of constituent elements.

1.5. Gay Lussac's law of gaseous volumes.

In 1808 Gay Lussac and Hambolt showed that under the same conditions of temperature and pressure 2 volumes of hydrogen combined with 1 volume of oxygen to produce 2 volumes of steam. From this experiment Gay Lussac concluded that in a gaseous reaction the reactants and the products were in a simple numerical ratio.

$$2H_2 + O_2 = 2H_2O$$

Here the ratio of the volumes of hydrogen, oxygen and steam is 2 : 1 : 2. Thus from a systematic study of a large number of gaseous reactions, Gay Lussac enunciated his famous law of gaseous volumes in 1808 which states—

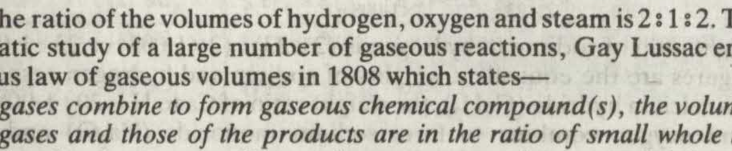
When gases combine to form gaseous chemical compound(s), the volumes of the reacting gases and those of the products are in the ratio of small whole numbers, measured under the same conditions of temperature and pressure. It is known as the **law of combining volumes of gases.**

Illustrations :

Under the same conditions of temperature and pressure it is found experimentally that,

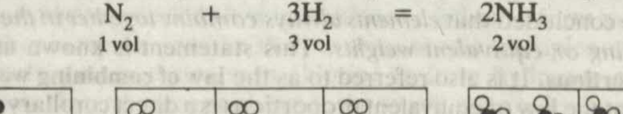
(i) 1 vol. of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia (ratio of volumes = 1 : 3 : 2).

$$\begin{array}{ccccc} 1\ \text{volume}\ N_2 & & 3\ \text{volume}\ H_2 & & 2\ \text{volume}\ NH_3 \\ N_2 & + & 3H_2 & = & 2NH_3 \\ 1\ \text{vol} & & 3\ \text{vol} & & 2\ \text{vol} \end{array}$$



(ii) 1 vol. of hydrogen and 1 volume of chlorine combine together to form 2 volumes of hydrogen chloride gas. The ratio of volumes of these gases is H : Cl : HCl = 1 : 1 : 2—a simple ratio.

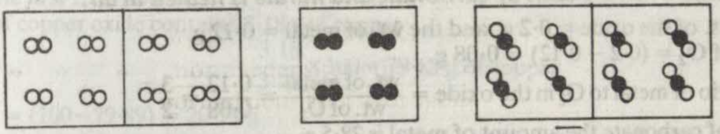
$$\begin{array}{ccccc} H_2 & + & Cl_2 & = & 2HCl \\ 1\ \text{vol} & & 1\ \text{vol} & & 2\ \text{vol} \end{array}$$



One atom Hydrogen=○, One atom Chlorine=●
One molecule of Hydrogen=○○
One molecule of Chlorine=●●
One molecule of Hydrogen Chloride=○●

(iii) 2 vols. of hydrogen react with 1 volume of oxygen to form 2 volumes of steam.

$$\underset{2\text{ vol}}{2H_2} + \underset{1\text{ vol}}{O_2} = \underset{2\text{ vol}}{2H_2O}$$



One atom H=○, One molecule H_2=○○
One atom Oxygen=●, One molecule of Oxygen=●●
One molecule of Steam=○●○

Thus, it can be experimentally shown that in every case the combining ratios of volumes of the reacting gases and products under the same conditions of temperature and pressure, are in the ratio of simple whole numbers.

As already mentioned earlier, the first four laws of stoichiometry describe the weight relationship between the reactants and products whereas Gay Lussac's law describes their volume relationship. Moreover, the first four laws were independent of temperature and pressure while Gay Lussac's law becomes meaningless without mentioning the identical conditions of temperature and pressure. It can be further pointed out that the first four laws can be accounted for by Dalton's atomic theory while Dalton's theory failed to explain Gay Lussac's law of combining volumes of gases.

1.6. Worked out Examples.

[A] **Problems on the law of conservation of mass.**

1. *3·0 g of ethane (C_2H_6) on complete combustion gave 8·8 g of CO_2 and 5·4 g of water. Show that these results illustrate the law of conservation of mass.*

Ans : Ethane on complete combustion gave CO_2 and H_2O according to the following equation

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O$$

Mol. wt. of $C_2H_6 = 24 + 6 = 30$
Gram molecular wt. of C_2H_6 = 30 g and gram molecular wt. of oxygen = 32 g
2×30 g of C_2H_6 reacts with 7×32 g of oxygen.

$\therefore$ 3 g of C_2H_6 reacts with $\frac{7\times32\times3}{2\times30} = 11{\cdot}2$ g of O_2

Total mass of reactants = wt. of C_2H_6 + wt. of O_2
= 3·0 + 11·2 = 14·2 g

Total mass of products = wt. of CO_2 + wt. of H_2O
= 8·8 + 5·4 = 14·2 g

Since the total mass of reactants = total mass of products, the results are in agreement with the law of conservation of mass.

2. *0·17 g of NH_3 on decomposition gives 0·14 g of nitrogen and 0·336 lit of hydrogen at N.T.P. Show that the results are in accordance with the law of conservation of mass. [Given 1 litre of hydrogen at N.T.P. weighs 0·09 g]*

Ans : Weight of 0·336 lit of hydrogen at N.T.P. = 0·336×0·09 = 0·03 g
$\therefore$ weight of products = weight of nitrogen formed + weight of hydrogen
= 0·14 + 0·03 = 0·17 g

The reactant NH_3 is also 0·17 g. Hence the results illustrate the law of conservation of mass.

[B] **Problems on the law of constant or definite proportions.**

3. *Analysis showed that (a) 0·20 g of oxide was formed by heating 0·12 g of a metal in air. (b) The carbonate and nitrate of the metal contained 28·5% and 16·2% of metal respecively. Applying the law of constant proportions, calculate the amount of metallic oxide when 1 g each of carbonate and nitrate is heated in air.*

Ans. : Wt. of the oxide = 0·2 g. and the wt. of metal = 0·12 g

∴ Wt. of $O_2 = (0{\cdot}2 - 0{\cdot}12) = 0{\cdot}08$ g.

So the ratio of metal to O_2 in the oxide = $\frac{\text{wt. of metal}}{\text{wt. of } O_2} = \frac{0{\cdot}12}{0{\cdot}08} = \frac{3}{2}$

In 100 g of carbonate the amount of metal is 28·5 g

In 1 g of carbonate the amount of metal is $\frac{28{\cdot}5}{100} = 0{\cdot}285$ g

Now according to the law of definite proportions we get

$$\frac{\text{wt. of metal}}{\text{wt. of } O_2} = \frac{3}{2} \quad \text{Or,} \quad \frac{0{\cdot}285}{\text{wt. of } O_2} = \frac{3}{2} \quad \text{Or, wt. of } O_2 = \frac{0{\cdot}285 \times 2}{3} = 0{\cdot}19\text{ g.}$$

Hence the wt. of oxide which can be obtained from 1 g of carbonate = wt. of metal + wt. of $O_2 = (0{\cdot}285 + 0{\cdot}19) = 0{\cdot}475$ g.

Again in 100 g of nitrate the amount of metal is 16·2 g

∴ ,, 1 ,, ,, ,, ,, ,, ,, ,, $\frac{16{\cdot}2}{100} = 0{\cdot}162$ g

In this case $\frac{\text{wt. of metal}}{\text{wt. of } O_2} = \frac{3}{2}$ or, $\frac{0{\cdot}162}{\text{wt. of } O_2} = \frac{3}{2}$

or, wt. of $O_2 = \frac{0{\cdot}162 \times 2}{3} = 0{\cdot}108$ g

Hence the wt. of oxide obtained from 1 g of the nitrate = wt. of metal + wt. of $O_2 = (0{\cdot}162 + 0{\cdot}108) = 0{\cdot}27$ g

4. *Stas prepared silver chloride in variety of ways. The results are tabulated below :—*

Sample No.	*Wt. of Ag (in g)*	*Wt. of AgCl (in g)*
I	*80·24*	*106·6*
II	*108·549*	*144·207*
III	*69·8974*	*92·8745*

Show that these are in agreement with the law of constant proportions.

Ans : *In Sample I :*

106·6 g of AgCl are obtained from 80·24 g of Ag

∴ 100 ,, ,, ,, ,, ,, ,, $\frac{80{\cdot}24}{106{\cdot}6} \times 100 = 75{\cdot}27$ g of Ag

Hence the wt. of $Cl_2 = (100 - 75{\cdot}27) = 24{\cdot}73$ g

In Sample II :

144·207 g of AgCl are obtained from 108·549 g of Ag

∴ 100 ,, ,, ,, ,, ,, ,, $\frac{108{\cdot}549}{144{\cdot}207} \times 100 = 75{\cdot}27$ g of Ag

Hence the wt. of $Cl_2 = (100 - 75{\cdot}27) = 24{\cdot}73$ g

In Sample III :

92·8745 g of AgCl are obtained from 69·8974 g of Ag

∴ 100 ,, ,, ,, ,, ,, ,, $\frac{69{\cdot}8974}{92{\cdot}8745} \times 100 = 75{\cdot}26$ g of Ag

Hence the wt. of $Cl_2 = (100 - 75{\cdot}26) = 24{\cdot}74$ g

Thus the percentage of Ag and Cl_2 in the 3 samples are the same. Hence the above results are in agreement with the law of constant proportions.

5. *3·18 g of copper were dissolved in concentrated HNO_3. The solution was evaporated to dryness and ignited when a residue of 3·98 g of CuO was left behind. Again when hydrogen gas was passed through 1·06 g copper oxide, 0·847 g of copper was formed. Illustrate the law of definite proportions from the above data.*

Ans : *In the first Experiment :*

3·98 g of copper oxide contains 3·18 g of copper

$\therefore$ 100 ,, ,, ,, ,, ,, $\frac{3\cdot18}{3\cdot98}\times100 = 79\cdot89$ g of copper

Wt. of $O_2 = (100-79\cdot89) = 20\cdot11$ g

In the second Experiment :

1·06 g of copper oxide contains 0·847 g of copper

$\therefore$ 100 ,, ,, ,, ,, ,, $\frac{0\cdot847}{1\cdot06}\times100 = 79\cdot9$ g of copper

Wt. of $O_2 = (100-79\cdot9) = 20\cdot10$ g

Thus in the first expt. the percentages of Cu and O_2 are 79·89 and 20·11 respectively.

In the second expt. the percentages of Cu and O_2 are 79·90 and 20·10 respectively.

Since the percentage composition of copper and oxygen remains constant in both the experiments, the results justify the law of definite proportions.

6. *1·316 g of zinc on heating in air gave 1·6394 g of zinc oxide. 1·30 g of zinc on treatment with nitric acid and subsequent ignition gave 1·62 g of zinc oxide. Pure and dry hydrogen was passed over 2·646 g of zinc oxide when 2·124 g of zinc were obtained. Show that these results are in accordance with the law of constant proportions.*

Ans : From the data given—

(a) weight of ZnO = 1·6394 g
weight of Zn = 1·316 g
weight of O_2 that combines with Zn = $(1\cdot6394-1\cdot316) = 0\cdot3234$ g

$$\therefore \frac{\text{wt. of Zn}}{\text{wt. of } O_2} = \frac{1\cdot316\text{ g}}{0\cdot3234\text{ g}} = 4\cdot069$$

(b) weight of ZnO = 1·62 g
weight of Zn = 1·30 g
weight of oxygen = $(1\cdot62-1\cdot30) = 0\cdot32$ g

$$\therefore \frac{\text{wt. of Zn}}{\text{wt. of } O_2} = \frac{1\cdot3\text{ g}}{0\cdot32\text{ g}} = 4\cdot062$$

(c) weight of ZnO = 2·646 g
weight of Zn = 2·124 g
Hence wt. of $O_2 = (2\cdot646-2\cdot124) = 0\cdot522$ g

$$\therefore \frac{\text{wt. of Zn}}{\text{wt. of } O_2} = \frac{2\cdot124\text{ g}}{0\cdot522\text{ g}} = 4\cdot068$$

The above 3 results show that the ratio of the weights of zinc to oxygen is almost same. Hence the results agree with the law of constant proportions.

7. *0·36 g of a metal on ignitions in air, is converted into 0·60 g of its oxide. The percentage of metal in its carbonate is 28·57. Calculate the amount of oxide which can be obtained when 1·0 g of the carbonate is strongly heated in air.* *[W.B.H.S. 1964]*

Ans : Wt. of the metal oxide = 0·60 g
Wt. of the metal = 0·36 g

Hence the wt. of oxygen that combines with metal = $(0\cdot60-0\cdot36) = 0\cdot24$ g.

In the metal oxide, $\frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{0.36\text{ g}}{0\cdot24\text{ g}} = \frac{3}{2}$

Again 100 g of metal carbonate contain 28·57 g of metal
1 " " " " contains 0·2857 g of metal
According to the law of constant proportions, the ratio of weights of metal to oxygen will remain constant in metallic oxide whatever may be its source.

$$\text{Thus } \frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{3}{2} \qquad \text{or, } \frac{0{\cdot}2857}{\text{wt. of oxygen}} = \frac{3}{2}$$

$$\therefore \text{ wt. of oxygen} = \frac{2\times 0{\cdot}2857}{3} = 0{\cdot}1905\text{ g}$$

Hence the wt. of metal oxide obtained from 1 g of carbonate
= wt. of metal + wt. of oxygen
= 0·2857 g + 0·1905 g = 0·4762 g.

8. *C is a compound. 30 g of C gave on analysis 10 g of an element A and 20 g of another element B. If 15 g of A react with 50 g of B, how much C will be formed and what will be the weight of the whole mixture ?* [*W.B.H.S. 1980*]

Ans : The ratio of the masses of the constituent elements *A* and *B* of the compound *C* will remain constant whatever may be the method of preparation of the compound *C* (Law of definite proportions).

Analysis of 30 g of the compound *C* shows :

$$\frac{\text{wt. of } A}{\text{wt. of } B} = \frac{10\text{ g}}{20\text{ g}} = \frac{1}{2}$$

In the Second case :

Suppose *x* g of *B* combines with 15 g of *A*.

$$\text{Hence in this case } \frac{\text{wt. of } A}{\text{wt. of } B} = \frac{15\text{ g}}{x\text{ g}} = \frac{15}{x}$$

But according to the law, it must be $\frac{1}{2}$

$$\therefore \frac{15}{x} = \frac{1}{2} \qquad \text{or, } x = 30$$

Hence the wt. of *B* = 30 g
Thus 15 g of *A* will combine with 30 g of B to form (15 + 30)=45 g of *C*
The wt. of the mixture = 45 g *C* + unreacted *B*
the wt. of unreacted *B* = 50 − 30 = 20 g.
.. the wt. of the mixture = 45 g of *C* + 20 g of unreacted *B* = 65 g

9. *An analysis of the North Sea water shows that 0·62 g of hydrogen is present per 5·58 g of water. 1·89 g of rain water contain 1·68 g of oxygen. Again 11·24 g of water are formed when 1·25 g hydrogen are ignited in air. Which law of stoichiometry is justified by the above experimental data ?*

Ans : 5·58 g of the North Sea water contain 0·62 g of hydrogen
$\therefore$ the wt. of O_2 = (5·58−0·62) = 4·96 g
1·89 g of rain water contain 1·68 g O_2
$\therefore$ the wt. of H_2 in rain water = (1·89 − 1·68) = 0·21 g.
Again on complete combustion 1·25 g H_2 yields 11·24 g H_2O
$\therefore$ the wt. of O_2 in 11·24 g H_2O = (11·24 − 1·25) = 9·99 g.
Now in sea water :

$$\frac{\text{wt. of oxygen}}{\text{wt. of hydrogen}} = \frac{4{\cdot}96\text{ g}}{0{\cdot}62\text{ g}} = \frac{8}{1}$$

In rain water :

$$\frac{\text{wt. of oxygen}}{\text{wt. of hydrogen}} = \frac{1{\cdot}68\text{ g}}{0{\cdot}21\text{ g}} = \frac{8}{1}$$

In combustion water :

$$\frac{\text{wt. of oxygen}}{\text{wt. of hydrogen}} = \frac{9{\cdot}99\text{ g}}{1{\cdot}25\text{ g}} = \frac{8}{1}$$

Thus the weights of hydrogen and oxygen in the three samples of water remain constant. The data are in conformity with the law of definite proportions.

10. *Ferrous sulphide contains 63·53% of iron. 4 g of iron are mixed with 2 g of sulphur and the mixture is strongly heated. Calculate how much ferrous sulphide will be formed.*

Ans : Percentage of sulphur in FeS = (100 − 63·53) = 36·47
According to the law of definite proportions the ratio of the wts. of Fe and S = 63·53 : 36·47
or, 36·47 g of S combine with 63·53 g of Fe

$$2 \text{ „ „ S } \text{ „ } \text{ „ } \frac{63{\cdot}53\times2}{36{\cdot}47} = 3{\cdot}484\text{ g of Fe}$$

∴ the unreacted Fe = (4 − 3·484) = 0·516 g.
Amount of FeS = 3·484 + 2 = 5·484 g.
The wts. of the total quantity of matter at the end of the reaction = 0·516 + 5·484
= 6·0 g.

[C] Problems on the law of multiple proportions

11. *A metal forms two oxides which contain 53·33% and 36·36% of oxygen respectively. Show that the results are in agreement with the law of multiple proportions.*

Ans : *In the First oxide :*
the wt. of oxygen = 53·33 g. So the wt. of metal = (100 − 53·33) = 46·67 g.
In the Second oxide :
the wt. of oxygen = 36·36 g. So the wt. of metal = (100 − 36·36) = 63·64 g.
Now 36·36 g of oxygen combine with 63·64 g of metal

$$53{\cdot}33 \text{ „ „ } \text{ „ } \text{ „ „ } \frac{63{\cdot}64\times53{\cdot}33}{36{\cdot}36} = 93{\cdot}34\text{ g of metal}$$

Thus the wts. of metals, i.e., 46·67 g and 93·34 g which combine with a definite wt. of oxygen, i.e., 53·33 g, are in a simple ratio 46·67 : 93·34 = 1 : 2

Thus the results are in agreement with the law of multiple proportions.

12. *Two elements A and B combine together to form 3 different compounds. The percentages of B in the 3 different compounds are 25·0, 14·28 and 7·69 respectively. Show that the results agree with the law of multiple proportions.*

Ans : In the first compound 25·0 g of *B* are present in 100 g of the compound. Hence the wt. of *A* = (100 − 25·0) = 75·0 g.
or, 25 g of *B* combine with 75 g of *A*

$$1 \text{ „ „ } B \text{ „ } \text{ „ } \frac{75}{25} = 3\text{ g of } A$$

In the second compound, the wt. of *B* = 14·28 g
Hence the wt. of *A* = (100 − 14·28) = 85·72 g
or, 14·28 g of *B* combine with 85·72 g of *A*

$$1 \text{ „ „ } B \text{ „ } \text{ „ } \frac{85{\cdot}72}{14{\cdot}28} = 6\text{ g of } A$$

In the 3rd compound, the wt. of *A* = (100 − 7·69) = 92·31 g and the wt. of *B*=7·69 g.
or, 7·69 g of *B* combine with 92·31 g of *A*

$$1 \text{ „ „ } B \text{ „ } \text{ „ } \frac{92.31}{7{\cdot}69} = 12\text{ g of } A.$$

Hence the wts. of *A* which combine with the same wt. (1 g) of *B* are 3 g, 6 g and 12 g. Their ratio = 3 : 6 : 12 = 1 : 2 : 4 (a simple ratio)

Thus the results agree with the law of multiple proportions.

13. ***A metal M forms two oxides. The oxide A contains 27·6% of oxygen and the oxide B contains 30% of oxygen. If the formula of A be M_3O_4, find that of B.***

(Cal. I. Sc. 1940)

Ans : ***In the first oxide A :***

The wt. of oxygen = 27·6 g. The wt. of metal M = (100 − 27·6) = 72·4 g.

Formula of *A* is M_3O_4. Let the atomic weight of metal be *x*.

$$\therefore \frac{\text{Number of atoms of M}}{\text{Number of atoms of oxygen}} = \frac{3}{4}\text{(by formula)} = \frac{\frac{72\cdot4}{x}}{\frac{27\cdot6}{16}} \text{ (16 is the at wt. of oxygen)}$$

$$\text{or, } x = \frac{72\cdot4\times16\times4}{27\cdot6\times3} = 55\cdot96$$

Thus the atomic weight of the metal is 55·96

In the second oxide B :

The wt. of metal = (100 − 30) = 70 g.

$$\therefore \frac{\text{Nubmer of atoms of M}}{\text{Number of atoms of O}} = \frac{70/55\cdot96}{30/16} = \frac{1\cdot25}{1\cdot875} = \frac{2}{3}$$

The ratio of atoms of M and O = 2 : 3

Hence, the fornula = M_2O_3

14. ***Two oxides of the metal M were heated to a constant weight in a stream of hydrogen. 2 g of each of the oxides gave 0·2517 g and 0·4528 g of water respectively. If the formula of the second oxide be MO what will be the formula of the first oxide ?***

Ans : **2 g of the first oxide on reduction give 0·2517 g of water.**

$$\therefore \text{1 g of the oxide gives } \frac{0\cdot2517}{2} = 0\cdot1258 \text{ g of water.}$$

$$\text{Similarly, 1 g of the second oxide gives } \frac{0\cdot4528}{2} = 0\cdot2264 \text{ g of } H_2O$$

We know,

18 g of water contain 16 g of oxygen

$$0\cdot1258 \text{ g of water contain } \frac{16}{18}\times0\cdot1258 = 0\cdot1118 \text{ g of Oxygen}$$

Thus, in the first oxide this amount of oxygen must be present.

So the wt. of metal M = (1·0 − 0·1118) = 0·8882 g.

Similarly the wt. of oxygen present in 0·2264 g of H_2O in the second oxide

$$= \frac{16}{18}\times0\cdot2264 = 0\cdot2012 \text{ g}$$

∴ The wt. of metal (M) in the second oxide = (1 − 0·2012) g = 0·7988 g

Let the atomic weight of the metal be *x*

The formula of the second oxide = MO

Hence, according to the formula,

$$\frac{\text{Number of atoms of M}}{\text{Number of atoms of oxygen}} = \frac{1}{1} = \frac{\frac{0\cdot7988}{x}}{\frac{0\cdot2012}{16}} \text{ or, } x = 63\cdot52$$

The atomic weight of the metal = 63·52

In the first oxide the ratio of atoms $= \dfrac{\dfrac{0{\cdot}8882}{63{\cdot}52}}{\dfrac{0{\cdot}1118}{16}} = \dfrac{2}{1}$

Hence the formula of the first oxide is M_2O.

15. *Chlorine and oxygen form 2 different compounds, one of them contains 81·6% and the other contains 59·7% of chlorine by weight. State the law of chemical combination which is in agreement with the experiment. Give arguments in support of your answer.* *(W.B.H.S. 1979)*

Ans : *In the first compound—*
The percentage of chlorine = 81·6 and the percentage of oxygen = 18·4
The ratio of the wts. of chlorine and oxygen = 81·6 : 18·4 = 4·43 : 1.
In the second compound—
The percentage of chlorine = 59·7 and the percentage of oxygen = 40·3
The ratio of the wts. of chlorine and oxygen = 59·7 : 40·3 = 1·48 : 1
Thus, the wts. of chlorine which combine with a fixed wt. of oxygen, i.e., 1, are in the ratio 1·48 : 4·43 or 1 : 3 (a simple ratio of whole number)
Hence the data illustrates the law of multiple proportions.
For the statement of the Law see the text book.

16. *A and B are two oxides of Tin. The oxide A contains 78·77% of Sn and 21·23% of oxygen while B contains 88·12% of Sn and 11·88% of oxygen. Show that the results agree with the law of multiple proportions.* *(I.I.T. 1975)*

Ans : *In the oxide A—*
21·23 parts by wt. of O_2 combine with 78·77 parts by wt. of tin
∴ 1 " " " " " combines " $\dfrac{78{\cdot}77}{21{\cdot}23} = 3{\cdot}7$ parts by wt. of tin
In the second oxide B—
1 part by wt. of O_2 combines with $\dfrac{88{\cdot}12}{11{\cdot}88} = 7{\cdot}4$ parts by wt. of tin
The ratio of the wts. of tin which combine with 1 part by wt. of $O_2 = 3{\cdot}7 : 7{\cdot}4 = 1 : 2$
Since it is a simple ratio, the data illustrate the law of multiple proportions.

17. *A metal forms two oxides. On heating 1 g of each in dry hydrogen 0·798 g and 0·888 g of the metal are formed respectively. Show that the results agree with the law of multiple proportions.* *(W.B.J.E.E. 1978)*

Ans : *In the first oxide—*
Wt. of metal = 0·798 g
Wt. of oxygen = (1 − 0·798) = 0·202 g
0·202 g of O_2 combines with 0·798 g of metal
or, 1 " " " " " $\dfrac{0{\cdot}798}{0{\cdot}202} = 3{\cdot}95$ g of metal.

In the second oxide—
Wt. of metal = 0·888 g
Wt. of oxygen = (1 − 0·888) = 0·112 g
0·112 g of O_2 combines with 0·888 g of the metal
or, 1 " " " " " $\dfrac{0{\cdot}888}{0{\cdot}112} = 7{\cdot}93$ g of the metal

Thus the ratio of the wts. of metal which combine with 1 g of $O_2 = 3{\cdot}95 : 7{\cdot}93 = 1 : 2$.
Since this is a simple ratio of whole number, the law of multiple proportions is established.

18. *Carbon combines with hydrogen to form three compounds A, B and C. The percentages of hydrogen in A, B and C are 25, 14·3 and 7·7 respectively. Which law of chemical combinations does this example illustrate ?* *(I.I.T. 1973)*

Ans : *In compound A—*
25 parts by wt. of hydrogen combine with 75 parts by wt. of carbon

1 part " " " " " combines " $\frac{75}{25} = 3$ parts by wt. of carbon

In compound B—
14·3 parts by wt. of hydrogen combine with 85·7 parts by wt. of carbon

1 part " " " " " combines " $\frac{85 \cdot 7}{14 \cdot 3} = 6$ parts by wt. of carbon

In compound C—
7·7 parts by wt. of hydrogen combine with 92·3 parts by wt. of carbon

1 part " " " " " combines " $\frac{92 \cdot 3}{7 \cdot 7} = 12$ parts by wt. of carbon

Thus, in *A*, *B* and *C*, the wt. ratio of carbon for a constant (i.e., 1 part) wt. of hydrogen = 3 : 6 : 12 or 1 : 2 : 3

This is a simple ratio of whole numbers. So, these data agree with the law of multiple proportions.

19. *Specimens of hydrocarbons were burnt in air. 0·016 g of one gives 23·9 ml of* CO_2 *and 0·052 g of the other hydrocarbon gives 95·8 ml of* CO_2*, both the volumes are measured at 15°C and 755 mm pressure. Show that these results are in agreement with the law of multiple proportions.*

Ans : *In the first hydrocarton—*
Let the volume of the given CO_2 at N.T.P. be V_2 ml.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{(From the combination of Charles and Boyle's Laws)}$$

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{755 \times 23 \cdot 9 \times 273}{760 \times 288} = 22 \cdot 5 \text{ ml}$$

We know,
In 22400 ml of CO_2 at N.T.P. the wt. of carbon = 12 g

" 22·5 " " " " " " $\frac{12 \times 22 \cdot 5}{22400} = 0 \cdot 012$ g

The weight of hydrocarbon = 0·016 g
$\therefore$ the wt. of hydrogen = 0·016 − 0·012 = 0·004 g
0·004 g H_2 combines with 0·012 g of carbon

$\therefore$ 1 " " " " $\frac{0 \cdot 012}{0 \cdot 004} = 3$ g of carbon

In the second hydrocarbon—

The vol. of the given CO_2 at N.T.P. = $\frac{755 \times 273 \times 95 \cdot 8}{760 \times 288} = 90 \cdot 22$ ml

The wt. of carbon in 90·12 ml CO_2 = $\frac{12 \times 90 \cdot 22}{22400} = 0 \cdot 048$ g

The wt. of hydrocarbon = 0·052 g
Wt. of hydrogen = 0·052 − 0·048 = 0·004 g
0·004 g of hydrogen combines with 0·048 g of carbon

1 " " " " " $\frac{0 \cdot 048}{0 \cdot 004} = 12$ g of carbon

So the wts. of carbon which combine with 1 g of hydrogen are in ratio 3 : 12 = 1 : 4. This ratio being simple, the data are in agreement with the law of multiple proportions.

20. *1·00 g of copper was dissolved in nitric acid and on ignition gave 1·25 g of cupric oxide. 1·00 g of cuprous oxide when heated in a current of hydrogen gave 0·888 g of copper. Show that these results illustrate the law of multiple proportions and calculate the percentage of copper in each case.* *(Cal I. Sc. 1949)*

Ans : In cupric oxide, the wt. of oxygen = (1·25 − 1·00) = 0·25 g
0·25 g of oxygen combines with 1 g of copper
1 " " " " " $\frac{1}{0{\cdot}25} = 4$ g of copper

In cuprous oxide the wt. of oxygen = (1·0−0·888) = 0·112 g
0·112 g of oxygen combines with 0·888 g of copper
1 " " " " " $\frac{0{\cdot}888}{0{\cdot}112} = 7{\cdot}92 \approx 8$ g of copper

Hence, the wts. of copper which combine with a fixed wt. of oxygen i.e., 1 g, are in the ratio 4 : 8 or 1 : 2 which is a simple ratio.
Thus the data agree with the law of multiple proportions.
In CuO, 1·25 g of oxide contain 1 g of Cu
∴ 100 " " " " $\frac{1 \times 100}{1{\cdot}25} = 80$

Thus the percentage of Cu in CuO = 80
In Cu_2O, 1 g of oxide contains 0·888 g of Cu
∴ 100 " " " contain $\frac{0{\cdot}888 \times 100}{1} = 88{\cdot}8$

The percentage of Cu in Cu_2O = 88·8.

[D] Problems on the law of reciprocal proportions.

21. *Phosphine contains 91·1% of P and 8·9% of hydrogen. Water contains 88·8% of oxygen and 11·2% of hydrogen, while phosphorous pentoxide contains 56·4% of P and 43·6% of oxygen. Show that these results illustrate the law of reciprocal proportions.*

Ans : *In* PH_3—
8·9 g of hydrogen combine with 91·1 g of phosphorous
1 " " " combines " $\frac{91{\cdot}1}{8{\cdot}9} = 10{\cdot}236$ g of phosphorus

In H_2O—
11·2 g of hydrogen combine with 88·8 g of oxygen
1 " " " combines " $\frac{88{\cdot}8}{11{\cdot}2} = 7{\cdot}928$ g of O_2

Therefore, phosphorous and oxygen should combine in the ratio 10·236 : 7·928 = 1 : 0·773
In P_2O_5, in fact, the ratio of P to oxygen = 56·4 : 43·6 = 1 : 0·773 or, the two ratios are the same.
Hence the data are in agreement with the law of reciprocal proportions.

22. *Show that the following figures illustrate a law of chemical combination. 0·14 g of an element A combines with 0·16 g of element B, while 0·05 g of another element C combines with 0·35 g of element A. 2·2857 g of element B combines with 0·285 g of element C.*

Ans : 0·14 g of *A* combines with 0·16 g of *B*
1 " " " " " $\frac{0{\cdot}16}{0{\cdot}14} = 1{\cdot}14$ g of *B*
∴ Ratio of the weights of *A* and *B* = 1 : 1·14 ······(i)
0·35 g of *A* combines with 0·05 g of *C*

1 g of *A* combines with $\frac{0{\cdot}05}{0{\cdot}35} = 0{\cdot}14$ g of *C*

∴ Ratio of the weights of *A* and $C = 1 : 0{\cdot}14$ ·······(ii)

Here, the wt. ratio of $B : C = 1{\cdot}14 : 0{\cdot}14 = 8 : 1$

Again, 0·285 g of *C* combines with 2·2857 g of *B*

1 " " " " " $\frac{2{\cdot}2857}{0{\cdot}285} = 8$ g of *B*

The weight ratio of $B : C = 8 : 1$ ·······(iii)

From (i) and (ii), it is found that the weight ratio of *B* and *C*, each of which combines separately with a fixed weight of *A*, (i.e., 1 g) is 8 : 1 which is the same as the original weight ratio of *B* and *C* as in (iii). Hence the results illustrate the law of reciprocal proportions.

23. *Carbon monoxide and aluminium carbide contain 27·27% and 25% of carbon respectively. Again aluminium oxide contains 47·1% of oxygen. Show that these figures agree with the law of reciprocal proportions.*

Ans : In CO, the wt. of oxygen = (100 − 27·27) = 72·73 g.

27·27 g of carbon combine with 72·73 g of oxygen

1 " " " " " $\frac{72{\cdot}73}{27{\cdot}27} = 2{\cdot}66$ g of oxygen

In Al_4C_3 the wt. of Al = (100·0 − 25·0) = 75·0 g

25 g of carbon combine with 75·0 g of Al

1 " " " " " $\frac{75}{25} = 3$ g of Al

∴ The combining weight ratio of oxygen and aluminium 2·66 : 3 = 1 : 1·12

Again, in Al_2O_3, the wt. of Al = (100 − 47·1) = 52·9 g.

Here the wt. ratio of oxygen and aluminium = 47·1 : 52·9 = 1 : 1·12

The wt. ratio being the same, the data are in agreement with the law of reciprocal proportions.

24. *Show that the following experimental data illustrate the three laws of stoichiometry.*

(a) 0·46 g Mg yields 0·77 g of MgO when it combines with oxygen. 760 ml of dry hydrogen gas is liberated at N.T.P. when 0·82 g of Mg reacts with cold, dilute H_2SO_4. 0·63 g water is obtained from 0·56 g of oxygen.

(b) 0·36 g of Mg forms 1·425 g of $MgCl_2$. On electrolysis of 4·75 g of fused $MgCl_2$ 1·12 litre of Cl_2 are liberated at N.T.P. at the anode.

(c) A and B are two oxides of a metal. On passing a stream of dry H_2 gas through 2 g of A, it is found that 0·2517 g of H_2O is obtained. Again on reduction by hydrogen 1 g B gives 0·2264 g of H_2O.

Ans : (*a*) 0·46 g of Mg yields 0·77 g of MgO

∴ Wt. of oxygen = (0·77 − 0·46) = 0·31 g

0·46 g of Mg combines with 0·31 g of O_2

∴ 1 " " " " " $\frac{0{\cdot}31}{0{\cdot}46} = 0{\cdot}67$ g of O_2

Wt. of 760 ml of H_2 at N.T.P. = 760 × 0·00009 = 0·0684 g

0·82 g of Mg displaces 0·0684 g of H_2

1 " " " " $\frac{0{\cdot}0684}{0{\cdot}82} = 0{\cdot}079$ g of H_2

Thus, it is evident that 0·079 g of hydrogen combines with 0·67 g of oxygen. So the weight ratio of hydrogen and oxygen is H : O = 0·079 : 0·67 = 1 : 8

Again given 0·56 g of O_2 gives 0·63 g of H_2O

Wt. of H_2 = (0·63 − 0·56) = 0·07 g

Thus the wt. ratio H : O = 0·07 : 0·56 = 1 : 8

Hence the above data are in conformity with the law of reciprocal proportions.

(*b*) Wt. of Mg = 0·36 g
Wt. of Cl_2 = (1·425 − 0·36) = 1·065 g
Wt. of Mg : Wt. of Cl_2 = 0·36 : 1·065 = 1 : 3

We know wt. of 22·4 litre Cl_2 at N.T.P. = 71 g

∴ " " 1·12 " " " " $= \frac{71 \times 1{\cdot}12}{22{\cdot}4} = 3{\cdot}55$ g

Hence the wt. of Mg = (4·75 − 3·55) = 1·2 g.

Here the wt. of Mg : wt. of Cl_2 = 1·2 : 3·55 = 1 : 3

Thus, the wt. ratio of the constituent elements of $MgCl_2$ i.e., Mg and Cl_2 is constant i.e., 1 3. The data are in agreement with the law of constant proportions.

(*c*) The wt. ratio of H_2 and O_2 in water is 1 : 8
or, 9 g of H_2O contain 8 g of O_2

∴ Wt. of O_2 in 0·2517 g of $H_2O = \frac{0{\cdot}2517 \times 8}{9} = 0{\cdot}2237$ g

Again, the wt. of metal in 2 g of *A* = (2− 0·2237) = 1·7763 g
or, 0·2237 g of O_2 combines with 1·7763 g of metal

1 " " " " " $\frac{1{\cdot}7763}{0{\cdot}2237} = 7{\cdot}94 \simeq 8$ g of metal

Again, the wt. of metal in 1 g of *B* = (1− 0·2) = 0·8 g
or, 0·2 g of O_2 combines with 0·8 g of metal

1 " " " " " $\frac{0{\cdot}8}{0{\cdot}2} = 4$ g of metal

Now keeping the wt. of oxygen constant, i.e., 1 g, the ratio of the different wts. of metal is 4 : 8 or 1 : 2, which is a simple ratio. The results thus are in agreement with the law of multiple proportions.

25. *0·6 g of a metal on reacting with acid produces 560 ml of hydrogen at N.T.P. and 0·12 g of the metal produces 0·20 g of oxide when burnt. Again 0·56 g of oxygen produces 0·63 g of water. Show that the above facts can be explained with the help of one law of chemical combinations.* *[W.B.H.S. '81]*

Ans : Wt. of 560 ml of H_2 at N.T.P. = 0·00009 × 560 = 0·0504 g
0·6 g of metal yields 0·0504 g of H_2

1 " " " " $\frac{0{\cdot}0504}{0{\cdot}6} = 0{\cdot}084$ g of H_2

Again, 0·12 g of metal combines with (0·2 − 0·12) = 0·08 g of O_2

1 " " " " " $\frac{0{\cdot}08}{0{\cdot}12} = 0{\cdot}67$ g of O_2

Hence the wt. ratio of H : O will be 0·084 : 0·67 or 1 : 7·97 ≃ 1 : 8

In water (0·63 − 0·56) = 0·07 g H_2 combines with 0·56 g of O_2 or the wt. ratio of H : O in water = 0·07 : 0·56 ≃ 1 : 8

Thus it is evident that the ratio of the wts. of hydrogen and oxygen each of which combines separately with a fixed wt. of the metal, is the same as the ratio in which they combine to produce water.

So the results are in accordance with the law of reciprocal proportions.

26. *A, B, and C are the three elements. 1 g of A combines with 1·33 g of B, 1 g of B combines with 0·125 g of C ; 1 g of C combines with 6·00 g of A. Show whether these results are in agreement with the law of reciprocal proportions.* *(W.B.H.S. '83)*

Ans : *In the first case—*
Wt. of $A = 1{\cdot}0$ g
Wt. of $B = 1{\cdot}33$ g
The weight ratio of A and $B = 1 : 1{\cdot}33$
In the second case—
Wt. of $B = 1{\cdot}0$ g
Wt. of $C = 0{\cdot}125$ g
The weight ratio of B and $C = 1 : 0{\cdot}125 = 8 : 1$
In the third case—
Wt. of $C = 1{\cdot}0$ g
Wt. of $A = 6$ g
The weight ratio of A and $C = 6 : 1$

In the second and the third cases the ratio of weights of A and B each of which combines separately with a fixed weight i.e., 1 g of C is $6 : 8$ or $1 : 1{\cdot}33$

This ratio is experimentally found in the first case. This agrees well with the law of reciprocal proportions.

[E] Problems on the Law of Gaseous Volume

27. *700 ml of gases were obtained when 500 ml of CO_2 were passed over white hot coke. All the volumes were measured under the same conditions of temperature and pressure. Find out the composition of the final gas mixture.*

Ans : The reaction between CO_2 and coke is

$$\underset{1\text{ vol}}{CO_2(g)} + C(s) = \underset{2\text{ vols}}{2CO(g)}$$

From the above equation it can be concluded that if the whole of CO_2 was converted into CO then the final volume would have been $2 \times 500 = 1000$ ml, but the final volume is 700 ml. This shows that in the final volume some unreacted CO_2 are present. Let x ml CO_2 take part in the reaction.

Hence the volume of CO from x ml $CO_2 = 2x$ ml

Hence the final volume at the end of the reaction will be $(500 - x)$ ml of CO_2 and $2x$ ml of CO.

The volume of two gases $= (500 - x) + 2x = 500 + x$

According to the problem

$500 + x = 700$ or, $x = 200$

$\therefore$ the volume of the unreacted $CO_2 = 500 - 200 = 300$ ml
and the volume of $CO = 2 \times 200 = 400$ ml.

28. *Calculate the volume of NH_3 when 100 ml of nitrogen combine with 400 ml of H_2 (the volumes being measured at N.T.P). Also find the volume of the final gas mixture.*

Ans : The synthesis of NH_3 takes place according to the following equation :

$$\underset{1\text{ vol}}{N_2(g)} + \underset{3\text{ vol}}{3H_2(g)} = \underset{2\text{ vol}}{2NH_3(g)}$$

According to the law of gaseous volume if the volume of nitrogen = 100 ml then the volume of $H_2 = 300$ ml and that of $NH_3 = 200$ ml.

or, 100 ml of nitrogen will combine with 300 ml of hydrogen to form 200 ml of NH_3

Hence the volume of $NH_3 = 200$ ml.

The volume of the given hydrogen being 400 ml, the volume of the unreacted hydrogen will be $400 - 300 = 100$ ml.

The whole of 100 ml of nitrogen will be completely consumed during the course of the reaction.

So the volume of the final gas mixture
= the volume of NH_3 formed + the volume of the unreacted hydrogen.
$= 200 + 100 = 300$ ml.

29. *Under the same conditions of temperature and pressure 2 volumes of O_3 on decomposition give 3 volumes of O_2. 20 ml of a gas mixture of O_3 and O_2 when heated and cooled expand to 21 ml. Find the percentage by volume of O_3 in the gas mixture.*

Ans : Let the volume of O_3 be x ml in the mixture.
$\therefore$ Vol. of $O_2 = (20 - x)$ ml
According to the problem 2 ml of O_3 form 3 ml of O_2
or, x ml O_3 form $3x/2$ ml of O_2

Hence $(20-x) + \frac{3x}{2} = 21$ or, $x=2$

$\therefore$ the vol. of $O_3 = 2$ ml.

The percentage of O_3 by volume $= \frac{2\times100}{20} = 10$

Hence 10% O_3 is present in the gas mixture.

1.7. Dalton's Atomic Theory — Constitution of Matter.

The concept that matter is composed of tiny discrete particles probably originated with the early Greek and Indian philosophers. In fact the word *atom* for such tiny particle originates from the Greek word—*A* (not) *tennein* (to cut) which means "not divided". It was **Sir John Dalton** (1808) who first started the ball of atomic theory to roll on a scientific path. The constitution of matter—the properties of atom, the concept of atomicity and the nature of atoms and how these atoms combine to form elements and compounds—all were the fundamental ideas of the atomic theory, known as *Dalton's atomic theory* which represented the greatest advancement that chemistry had yet made in the course of its development into a science. For this reason Dalton is known as the father of modern atomic theory.

Sir John Dalton

- **Postulates of Dalton's atomic theory :**

1. *Matter is composed of a large number of minute particles called atoms.*

Atoms are so small that it is impossible to conceive their volumes, e.g., the weight of a hydrogen atom is $1{\cdot}67\times10^{-24}$ g while its diameter is 12×10^{-9} cm.

2. *Atoms do not undergo subdivision during chemical reactions. They are incapable of being created or destroyed. Atoms are indivisible and indestructible.*

3. *Atoms of the same element are identical with each other in weight, size and other properties.*

4. *Atoms of different elements are different in all respects.*

5. *Chemical compounds are formed by the union of different elements in simple numerical proportions i.e., in simple ratio of whole numbers e.g., 1 : 1, 1 : 2, 2 : 3, etc. Since atoms are indivisible, they never combine in fraction.* Thus in water, the ratio of the atoms of hydrogen to oxygen is 2 : 1, in CO_2 the ratio of atoms of carbon and oxygen is 1 : 2 etc.

6. *The smallest particle of an elementary substance is called "simple atom" while that of a chemical compound "compound atom".* The combining weights of the elements or compounds represent the combining weights of simple atoms.

1.8. Utility of Dalton's Atomic Theory.

1. The correct definition of atom as the smallest indivisible material particle that takes part in a chemical reaction was first given by Dalton's Atomic Theory.

2. The theory can explain the mode of formation of all elementary substances through the union of atoms.

3. It explains how a chemical compound is formed by the union of elementary simple atoms.

4. The atomic theory successfully explains the laws of chemical combinations, with the exception of the law of gaseous volumes.

5. The postulate of atomic theory which states that the atoms of the same element are identical in mass and properties, helps to express the molecular weight of a compound and as a result the translation of a chemical reaction into chemical equation and chemical calculations have become much easier.

6. The atomic theory may be regarded as a precursor to Avogadro's hypothesis. The law of gaseous volumes can be explained with the help of atomic theory coupled with Avogadro's hypothesis.

[According to the fifth postulate of Dalton, the atoms in a compound always exist in a simple ratio of whole numbers. The compounds are rigorously stiochiometric. These are termed as *Daltonide compounds*, e.g., CuO, Fe_2O_3, CO_2 etc. Recently a number of solid compounds have been discovered, the exact analytical composition of which deviates from those predicted by atomic theory. The atoms in these compounds exist in fractions. These are known as *Berthollide compounds*, e.g., $Cu_{1.7}S$, $Fe_{0.88}S$ etc.]

1.9. Limitations of Dalton's atomic theory.

1. At present Daltonian concepts of atom have gone a thorough and radical change. It is now proved that an atom is composed of smaller particles like electrons, protons, neutrons, positrons etc. Modern discoveries proved that the atoms get divided during nuclear reactions. Thus, atom is no longer the fundamental particle of matter and the indivisibility of atom is no longer valid.

2. Compounds are no longer accepted as to be formed by the union of atoms. Chemical reactions result either by sharing or transfer of electrons. The nuclei of different atoms undergoing chemical changes remain uneffected.

3. The idea that the atoms of the same element are identical with each other in mass and properties, can no longer be held correct with the discovery of isotopes. Thus, hydrogen has 3 isotopes of mass numbers 1, 2 and 3. The chemical properties of these three isotopes are identical but their weights are different.

4. Dalton's atomic theory fails to explain the law of gaseous volumes.

5. After the discovery of *Isober* it was found that atoms of different elements may have identical weight. Thus, Ca^{40} and Ar^{40} are two different elements but their masses are identical.

6. The atomic weight of elements, the correct molecular formula of chemical compound cannot be ascertained by Dalton's atomic theory.

7. Although Dalton conceived the "simple atoms" for element and "compound atoms" for compound, the nature and the properties of the latter especially in chemical reactions were not properly elaborated. Moreover, the ultimate particle which is capable of free existence, was not mentioned in the atomic theory, i.e., the theory did not contain the concept of molecule.

In conclusion it may be recalled that there was a gradual development in the idea of fundamental particles of matter. Before the Daltonian era, 'element' was the ultimate particle which could not be further subdivided. During Dalton's time, atom was the fundamental particle of matter. But today, Dalton's tiny real discrete particle atom is shatterred into electron, proton, neutron, positron etc., and now they are the fundamental particles. Thus, although Dalton is regarded as the *father of atomic theory*, he is but a history to the modern scientists.

1.10. Explanations of the Laws of Stoichiometry in the light of Dalton's.

(1) The law of conservation of mass and atomic theory :

Since matter is composed of atoms which can neither be created nor destroyed, the total number of atoms present at the beginning of a chemical change must also be present at the end of the reaction. Again each atom has a fixed mass. So the total mass present at the beginning of chemical reaction remains the same after the reaction, e.g., water is formed when hydrogen burns in air.

$$2H_2 + O_2 = 2H_2O$$

The numbers of atoms of hydrogen and oxygen are 4 and 2 respectively. The total number of atoms of the reactant is $4 + 2 = 6$. When the reaction is complete, the numbers of hydrogen and oxygen atoms remain the same and their sum is 6.

Again the total weight of the atoms of hydrogen and oxygen $= (4\times1) + (2\times16) = 36$.
The weight of 2 molecules of water $= 2\,(2+16) = 36$.

Thus, the law of conservation of mass is explained easily from Dalton's atomic theory.

(2) Atomic theory and the law of constant or definite proportions :

Let x atoms of an element A combine with y atoms of an element B to form a compound A_xB_y.

Let a and b be the atomic weights of A and B respectively.

In the compound A_xB_y, 'ax' parts by weight of A combine with 'by' parts by weight of B to form A_xB_y.

Hence the weight ratio of A and B in the compound $A_xB_y = \dfrac{ax}{by}$

In accordance with the Dalton's atomic theory atoms combine to form a chemical compound in a simple ratio of whole numbers. Hence x and y must be simple integer. Again atoms of the same element are alike in all respects. Hence the atomic weights 'a' and 'b' of the two elements A and B are fixed. Since a, b, x and y are constants, the weight ratio $\dfrac{ax}{by}$ must be constant in the compound A_xB_y

This is the law of constant proportions.

(3) Atomic theory and the law of multiple proportions :

Let a and b be the atomic weights of the two elements A and B. In explaining the law of multiple proportions from the postulates of Dalton's atomic theory, let us assume that A and B combine together to form two different compounds A_xB_y and A_cB_d.

The weight ratio of A and B in $A_xB_y = ax : by$

$$\text{or,} \quad a = \frac{by}{x}$$

Again in A_cB_d the weight ratio of A and $B = ac : bd$

$$\text{or,} \quad a = \frac{bd}{c}$$

Now the ratio of the weights of B which combines with a fixed weight of the element A i.e., a

$$= \frac{by}{x} : \frac{bd}{c} :: cy : dx$$

(since b is constant according to the atomic theory)

Again in accordance with the atomic theory c, d, x and y are whole numbers i.e., $cy : dx$ is a simple ratio. Thus the law of multiple proportions is established.

(4) Atomic theory and the law of reciprocal proportions :

Let us assume that m atoms of the element A and n atoms of the element B separately combine with p atoms of the element C to form the compounds A_mC_p and B_nC_p respectively. Again x atoms of A combine with y atoms of B to form the compound A_xB_y. Since according to the Dalton's atomic theory chemical reactions take place by the union of atoms in simple definite numerical proportions, the ratios (i) m/p, (ii) n/p and (iii) x/y are all simple. The ratio m/n which is obtained by dividing (i) by (ii) should be simple and must bear a relation with the other simple ratio x/y or in other words either m/n and x/y are equal or one is the multiple of the other.

Let a, b and c be respectively the atomic weights of the elements A, B and C then—

(1) In the two compounds A_mC_p and B_nC_p, 'am' parts by weight of A and 'bn' parts by weight of B combine separately with a definite weight cp of C.

(2) In the compound A_xB_y, the 'ax' parts by weight of A combines with 'by' parts by weight of B. According to the law of reciprocal proportions, either the two ratios $\frac{am}{bn}$ and $\frac{ax}{by}$ are the same or one is the multiple of the other.

It is already proved that the ratios m/n and x/y are either the same or one is the multiple of the other.

Now multiplying the two ratios by a/b, we get, $\frac{am}{bn}$ and $\frac{ax}{by}$. Hence these two ratios must be the same or one is the multiple of the other.

Thus, the law of reciprocal proportions is established.

1.11. Concept of atomic weight or atomic mass.

The weight or the mass of an atom is so negligible that it is not possible to weigh an atom in a chemical balance. Indirect calculations show that the actual weight of one atom of the lightest element hydrogen is $1{\cdot}67\times10^{-24}$ g while that of heaviest element uranium is only $3{\cdot}95\times10^{-22}$ g. Hence is the necessity of determining the weights of atoms with reference to the weight of an atom of a standard element, or in other words atomic weight or atomic mass refers to the relative atomic weight. It is this relative weight which is known as atomic weight of an element.

Thus, *the atomic weight of an element is a number which indicates how many times heavier an atom of the element is, in comparison to an atom of another element taken as a standard.*

$$\text{or, The atomic weight of an element} = \frac{\text{weight of 1 atom of the element}}{\text{weight of 1 atom of a standard element}}$$

1. Hydrogen scale :

The atomic weight of an element is a pure number which shows how many times the weight of one atom of the element is heavier than the weight of one atom of hydrogen, the weight of it being taken as unity.

$$\text{The atomic weight of an element} = \frac{\text{Weight of 1 atom of the element}}{\text{Weight of 1 atom of hydrogen}}$$

"The atomic weight of carbon = 12"—It means that 1 atom of carbon is 12 times heavier than 1 atom of hydrogen.

2. Oxygen scale :

The definition of atomic weight has now been replaced by one based on the oxygen scale where $\frac{1}{16}$th part of the weight of an oxygen atom being taken as unit of comparison.

The atomic weight of an element is the weight of an atom of the element relative to the weight of one atom of oxygen which is taken as 16·0000. In other words,—the atomic weight of an element indicates how many times an atom of the element is heavier than 1/16th part of the weight of an oxygen atom.

$$\text{Atomic weight} = \frac{\text{weight of an atom of the element}}{\frac{1}{16}\text{th part of the weight of an oxygen atom.}}$$

$$= \frac{\text{weight of an atom of the element}}{\text{weight of an oxygen atom}} \times 16$$

'The atomic weight of carbon is 12'—means that an atom of carbon is 12 times heavier than $\frac{1}{16}$th part of an oxygen atom.

• Reasons for taking oxygen atom as standard.

(i) Since most of the elements especially the metals combine with oxygen rather than hydrogen to form stable compounds, determination of their atomic weights on the basis of hydrogen scale created problems.

(ii) Hydrogen is the lightest element, and hence the experimental errors in the determination of atomic weight of an element are magnified in terms of hydrogen scale.

(iii) The atomic weights of most of the elements based on hydrogen scale are found to be fractional, whereas the atomic weights of most elements come to whole numbers or very near to whole numbers when oxygen is taken as standard.

3. Carbon scale :

The atomic weight of an element indicates how many times an atom of the element is heavier than $\frac{1}{12}$th part of the weight of an atom of carbon 12 isotope.

$$\therefore \text{Atomic weight} = \frac{\text{weight of an atom of the element}}{\text{weight of an atom of C-12 isotope}} \times 12$$

According to this scale the atomic weight of hydrogen is 1·00796.

Atomic weight of an element does not signify the actual weight of an atom of the element. Since the atomic weight of an element is a ratio, it has no unit—it is only a number.

• Reasons for accepting C-12 as standard instead of oxygen.

The oxygen 16·0000 standard for the determination of atomic weight was in use until 1961. At present C-12 isotope has been taken as standard instead of oxygen. This was due to the discovery of isotopes of oxygen. After the discovery it was found that ordinary oxygen consists of a mixture of three isotopes—O^{16}, O^{17} and O^{18}. Consequently oxygen-16 standard was then found to be unsuitable as the standard (O=16) itself represented an average weight of the mixture of the three isotopes which constituted the ordinary oxygen. Hence the atomic weight of any element would depend on the isotopic composition of oxygen. So an attempt was made to select a single isotope of an element which would remain constant and could be employed as standard. Thus carbon-12 isotope was selected to use as standard for the determination of the atomic weights of elements.

• Gram atomic weight or gram atom :

When the atomic weight of an element is expressed in grams, it is known as gram atomic weight or gram atom.

Since gram atom indicates a quantity in grams which is equal to the atomic weight of an element, it has a unit. Scientifically, *gram atom of an element is defined as the weight in grams that contains the same number of atoms as 12 g of carbon-12 isotope.*

1 gram atom of oxygen refers to 16 g of oxygen and 1 gram atom of carbon = 12 g of carbon. 0·5 gram atom of carbon = 0·5 × 12 = 6 g of carbon.

1 gram atom of an element also refers to the weight in gram of $6{\cdot}023 \times 10^{23}$ *atoms of the element (Avogadro's number).*

1.12. Atomic mass unit or a.m.u.

All atoms have a definite weight or mass. *The unit in comparison with which the actual mass of an atom of an element is expressed, is called atomic mass unit or a.m.u.*

(i) According to oxygen scale :

$$1 \text{ atomic mass unit} = \frac{1}{16} \times \text{mass of 1 atom of oxygen } (O^{16})$$

From Avogadro's hypothesis,
we know 16 g of oxygen contain $6{\cdot}023 \times 10^{23}$ atoms of oxygen
or, $6{\cdot}023 \times 10^{23}$ atoms of oxygen weigh 16 g

$$1 \text{ atom of oxygen weighs } \frac{16}{6{\cdot}023 \times 10^{23}} \text{ g} = 2{\cdot}66 \times 10^{-23} \text{ g}$$

$$\text{Then 1 a.m.u.} = \frac{1}{16} \times \text{mass of 1 oxygen atom}$$

$$= \frac{1}{16} \times 2{\cdot}66 \times 10^{-23} \text{ g} = 1{\cdot}6603 \times 10^{-24} \text{ g}$$

(ii) According to the carbon scale (C^{12}) :

$$1 \text{ a.m.u.} = \frac{1}{12} \times \text{mass of 1 carbon atom}$$

$$= \frac{1}{12} \times \frac{12}{6{\cdot}023 \times 10^{23}} = 1{\cdot}6603 \times 10^{-24} \text{ g}$$

On this basis, mass of 1 hydrogen atom = 1·008 a.m.u.

$$= 1{\cdot}008 \times 1{\cdot}6603 \times 10^{-24} \text{ g}$$
$$= 1{\cdot}673 \times 10^{-24} \text{ g}$$

Mass of 1 nitrogen atom = 14 a.m.u. = $14 \times 1{\cdot}6603 \times 10^{-24}$ g
" " 1 carbon " = 12 a.m.u. = $12 \times 1{\cdot}6603 \times 10^{-24}$ g.

Thus *on multiplying the atomic weight of an element with one atomic mass unit the exact mass of one atom of the element can be found out.*

1.13. Physical and chemical scales of atomic weight.

When the atomic weight of an element is determined either on the basis of the hydrogen scale (H=1) or on the basis of oxygen (O=16) the result is known as *chemical atomic weight.*

Thus *the scale of atomic weight taking the weight of natural oxygen as 16·0000 is known as chemical atomic weight scale.*

In 1929 Vickey and Johnston proved that natural oxygen consisted of 3 isotopes of mass numbers 16, 17 and 18. In natural oxygen their percentages are 99·575, 0·039 and 0·204 respectively.

Hence the true weight of natural oxygen is

$$= 16 \times 0{\cdot}99575 + 17 \times 0{\cdot}00039 + 18 \times 0{\cdot}00204 = 16{\cdot}00447$$

F.W. Aston introduced a new scale, *Physical atomic weight* scale, for the determination of the atomic weight of an element. According to him only the O^{16} isotope of the natural oxygen was taken as a standard of reference. Thus, *the scale of atomic weight with* O^{16} *isotope of relative weight 16·0000 taken as standard of* *reference is called the physical atomic weight.* Hence a value of 16 in the chemical atomic weight scale corresponds to 16·00447 of the physical atomic weight scale.

$$\frac{\text{Physical atomic weight}}{\text{Chemical atomic weight}} = \frac{16{\cdot}00447}{16{\cdot}00000} = 1{\cdot}000272.$$

Thus, the physical atomic weight of an element is always higher than its chemical atomic weight by a factor of 1·000272. The chemical atomic weight scale is used by chemists whereas physicists prefer to use the physical atomic weight scale.

Thus the existence of the two atomic weight scales created much confusion among physicists and chemists. Hence in 1961, the international union of pure and applied chemistry replaced the O^{16} isotopes of oxygen by C^{12} isotope of carbon as the basis for atomic weight definition. This new scale has reduced considerably the discrepancy between the two scales. The following table reveals the differences among the three scales.

Species	Chemical atomic weight	Physical atomic weight	Atomic weight on the basis of C^{12} scale
H (natural)	1·008011	1·008288	1·007967
C (natural)	12·011617	12·014921	12·011150
O (natural)	16·000000	16·004470	15·999312
H—1	1·007865	1·008142	1·007822
O—16	15·995601	16·000000	15·994912
C—12	12·000516	12·003816	12·000000

1.14. Atomic-molecular theory.

Dalton's Atomic theory failed to explain the Gay Lusaac's law of gaseous volumes which was clearly accounted for by the Avogadro's hypothesis (to be discussed in chapter 2). As a result of this, Dalton's theory was substantially modified by Avogadro and the new idea is known as *Atomic-moleculer theory*. The theory states :

1. The ultimate particles of matter which can exist in the free state are called molecules. The properties of the molecules are the properties of the matter.

2. The molecules are composed of indivisible particles called atoms. Again the molecules of elements are composed of same atoms. These molecules are known as *Elementary molecules*. The molecules of a compound are composed of different types of atoms. These molecules are referred to as *Compound molecules*.

3. The molecules of a particular substance are similar to one another in all respects but the molecules of one substance are entirely different from the molecules of another substance.

4. The moleculer weight of a substance is the sum total of the atomic weights of the constituent atoms.

5. During chemical reaction the atoms combine together in a simple numerical proportion to form molecules.

6. When chemical combination takes place between 2 or more substances, the molecules of each substance first spilt into *atoms* and then recombine to produce new *molecules* having different properties.

• Exercises •

1. What is meant by laws of stoichiometry ? Explain the relation of atoms with these laws.

2. State the law of conservation of mass. Show that the following observations do not contradict the law of conservation of mass—(a) The weight of a burning candle is decreased, (b) When a piece of coal is burnt in air its weight is decreased, (c) A magnesiun ribbon on burning in air increases in weight. (d) A piece of Iron when kept in moist atmosphere is increased in weight.

3. "The law of conservation of mass is not always true". Do you agree with this statement ? Explain with illustration.

2·45 g of $KClO_3$ yielded 1·49 g of KCl and 672 ml of oxygen at N.T.P. Show that these results are in accordance with the law of conservation of mass.

4. Explain the law of conservation of mass in the light of Dalton's Atomic theory.

In an experiment 0·5 g of $CaCO_3$ on heating gave 280 mg of CaO and 0·112 lit of CO_2 at N.T.P. Show that the results agree with the law of conservation of mass.

5. State and illustrate the law of definite proportions. Is the converse of the law of definite proportions always true ? Explain with illustrations. (*W.B.H.S.* '*95*)

6. Prove with the help of an experiment that the law of constant proportions is correct.

1·098 g of metallic copper is formed when dry hydrogen is passed over 1·375 g of cupric oxide. In another experiment, 1·179 g of metallic copper is dissolved in concentrated HNO_3, evaporated to dryness and strongly heated when it gives 1·476 g cupric oxide. Show that the results are in agreement with the law of constant proportions.

7. Silver chloride contains 75·26% silver. Calculate, on the basis of the law of definite proportions, the amount of silver required to produce 15 g of silver chloride. [*Ans.* 11·289 g]

8. On analysis it is found that FeS contains 36·47% of sulphur. How much FeS will be obtained on heating a mixture of 1 g of iron and 2 g of sulphur ? How much of sulphur remains undecomposed ?
[*Ans.* FeS = 1·574 g ; Undecomposed sulphur = 1·426 g]

9. Hydrated copper sulphate crystals contain 25·45% copper and 36·07% water. Calculate the amount of copper required to obtain 8·316 g of copper sulphate crystal applying the law of constant proportions. Find the amount of water present in the crystal. [*Ans.* copper = 2·116 g and water = 2·99 g]

10. (a) Nitrous oxide contains 63·64% by weight of nitrogen and NH_3 contains 17·65% by weight of hydrogen. What would be the weight of oxygen combining to 1 g of hydrogen in a compound of hydrogen and oxygen ? Does this result agree with the fact that in water 1 g of hydrogen combines with 8 g of oxygen ? [*Ans.* 2·67g or its multiple] [*W.B.H.S.* '*97*]

(b) Two oxides of element 'A' contains 27·5% and 30% oxygen respectively. The formula of second one is A_2O_3. Calculate the formula of the first one. [*Ans.* A_3O_4] [*W.B.J.E.* '*96*]

11. State the law of multiple proportions. Give examples. How would you verify the law experimentally ? Explain the law of multiple proportions on the basis of Dalton's atomic theory.
[*W.B.H.S.* '*95*] [*I.S.C. 1992*]

12. Critically examine the following statements.

(a) The five oxides of nitrogen are typical illustrations of the law of multiple proportions.

(b) Iron forms 3 oxides namely FeO, Fe_2O_3 and Fe_3O_4. The law of multiple proportions governs their formation. (*W.B.H.S.* '*93*)

(c) The law of multiple proportions fails in some cases. (*W.B.H.S. 1978,* '*84*)

13. Show that the following results illustrate a particular law of chemical combinations :

(a) The percentages of hydrogen in 3 compounds of nitrogen and hydrogen are 17·65, 12·50 and 2·33 respectively.

(b) The percentages of nitrogen in the two oxides of nitrogen are 63·65 and 46·68.

(c) The percentages of carbon by weight in two hydrocarbons are 75 and 80.

(d) The two chlorides of a metal *M* contain 35·9% and 52·8% of chlorine.
[*Ans.* = The law of multiple proportions]

14. Which law of chemical combinations will agree with the following experimental results :

0·347 g and 0·278 g of lead chloride are obtained separately in two different experiments from 0·257 g and 0·207 g of lead respectively. [*Ans.* Law of definite proportions]

15. The following observations were made when dry hydrogen gas was passed through some oxides of lead. Prove that the results agree with the law of multiple proportions.

(a) 1·393 g litharge yielded 1·293 g of lead.

(b) 21·73 g of lead peroxide yielded 1·882 g of lead.

(c) 1·712 g of red lead yielded 1·552 g of lead. (*W.B.H.S. 1974*)

16. (i) State the law of reciprocal proportions and illustrate it with suitable examples. Explain how the idea of equivalent weight follows as a consequence of this law.(*W.B. Joint Ent. 1979, W.B.H.S.* '*94,* '*97*)

(ii) Explain the law of reciprocal proportions in the light of the atomic theory of Dalton.
(*W.B.H.S.* '*94*)

17. 0·12 g of Mg produces 0·2 g of MgO. 0·6 g of Mg at N.T.P. yields 560 ml of dry hydrogen. Again 0·56 g of oxygen is required to produce 0·63 g of water. Which law of chemical combination is confirmed by the above data ? [*Ans.* Law of reciprocal proportions]

18. State Gay Lusaac's law of gaseous volumes and explain it with suitable examples. What is the difference between this law and the other four laws of chemical combinations ?

19. Explain the statement "Gay Lussac's law of gaseous volumes suggests that except the inert gases the elementary gases do not exist in the atomic state."

20. State the law of chemical combinations which agrees with the following observations. Explain the law with the help of Dalton's atomic theory.

(i) 0·48 g of Mg on oxidation yields 80 g of MgO.

(ii) 0·84 g of Mg on reaction with dilute HCl produces 784 ml of dry H_2 at N.T.P.

(iii) 1·26 g of water are produced when 1·12 g of O_2 combines with excess hydrogen.

[**Ans.** Law of reciprocal proportions] (*W.B. Joint Ent. 1980*)

21. A metal *M* has two oxides. On heating 1·0 g of each oxide with dry hydrogen gas 0·798 g and 0·888 g of metal were obtained. Show that the results are in agreement with the law of multiple proportions. (*W.B. Joint Ent. '64, '78*)

22. Two elements *A* and *B* combine with each other and form two compounds containing 88·88% and 94·12% of *B*. Show that these data are in agreement with the law of multiple proportion. [*W.B.H.S. '95*]

23. The percentage of nitrogen in a compound is 5·37. What is the minimum molecular weight of the compound ? [**Ans.** 260·7] (*I.I.T. 1969*)

24. 3·0 g of an element *X* combines with 2 g of an element *Y* to produce 5·0 g of a compound *Z*. Calculate how much *Z* will be formed when 48 g of *X* combine with 50 g of *Y*. Which element will be in excess ? [**Ans.** *Z*=80 g ; Excess *Y*=18 g]

25. Metal M and chlorine combine in different proportions to form two compounds *X* and *Y*. The mass ratios M : Cl=0·895 : 1 in *X* and 1·791 : 1 in *Y*.

(a) Which law of chemical combine does this example illustrate ? How ?

(b) Which of the following pairs of formulae is correct on the basis of the above information alone ?

	Compound *X*		Compound *Y*
(i)	MCl	and	M_2Cl
(ii)	MCl	and	MCl_2
(iii)	MCl_2	and	MCl
(iv)	MCl_3	and	M_2Cl_3

[**Ans.** (a) The law of multiple proportions ; (b) (i) MCl, M_2Cl ; (ii) MCl_2, MCl ; (iii) MCl_3, M_2Cl_3]

26. 15 g of a compound *C* on analysis yield 5 g of an element *A* and 10 g of another element *B*. Find the weight of *C* when 2·5 g of *A* and 5·25 g of *B* are mixed together. Find also the weight of the total mixture. [**Ans.** C=7·5 g ; Mixture=7·75 g]

27. Chlorine and oxygen combine to form two compounds. The first compound contains 81·6% of chlorine and the second compound contains 59·7% of chlorine. Which law of chemical combination satisfies the above result ? State the law and explain it with the help of Dalton's atomic theory.

[**Ans.** The law of multiple proportions] (*W.B.H.S. 1979*)

28. 0·6 g of a metal on reacting with acid produces 500 ml of hydrogen at N.T.P. and 0·12 g of the metal produces 0·20 g of oxide when burnt. Again 0·56 g of oxygen produces 0·63 g of water. Show that the above facts can be explained with the help of a law of chemical combination. State the law.

[**Ans.** The law of reciprocal proportions] (*W.B.H.S. 1981*)

29. Aluminium oxide contains 52·9%, Al and CO_2 contain 27·27% carbon. Assuming the law of reciprocal proportions, calculate the percentage of Al in aluminium carbide. [**Ans.** =75·01%] (*A.I.H.S. 1973*)

30. Show that the following results agree with the law of chemical combination. State the law.

(i) 0·14 g of an element *A* combines with 0·16 g of an element *B* to produce the compound *AB*. The compound *AC* is formed by the combination of 0·35 g of *A* and 0·05 g of *C*. Again 2·2857 g of *B* reacts with 0·0285 g of *C* to form the compound *BC*. (*H.S. Delhi—1967*)

[**Ans.** The law of reciprocal proportions]

31. Two oxides of metal (M) contain 72·4% and 70% of M respectively. If the formula of the first oxide be M_3O_4, determine the formula of the second oxide. [**Ans.** M_2O_3]

32. Under the same conditions of temperature and pressure 20 litre of the gas A combine with 60 litre of B to produce 40 litre of AB_3. How much AB_3 will be formed when 30 litre of A combine with 75 litre of B under the same conditions of temperature and pressure ? How much of the other unreacted constituent will be present in the mixture ? [**Ans.** Vol. of AB_3=50 litre ; Unreacted A=5 litre]

33. Oxygen combines with nitric oxide according to the following equation :

$$2NO + O_2 = 2NO_2$$

How much oxygen at N.T.P. and at 750 mm pressure and 20°C will be required to produce 3 litre of NO_2 ? [*Ans.* 1·5 litre and 1·63 litre]

34. Ammonia contains 82·35% nitrogen, water contains 11·11% hydrogen and hydrogen peroxide contains 69·57% oxygen. Show that the above results can be interpreted with the help of a law of chemical combination. State the law. [*Ans.* Law of reciprocal proportions] (*W.B.H.S. 1985*)

35. Air contains 21% oxygen by volume. Calculate the theoretical volume of air which will be required for burning completely 500 ml of Acetylene. All volumes are measured under the same condition of temperature and pressure. [*Ans.* 5952.38 ml]

36. 24 ml of Methane were mixed with 106 ml of oxygen and the mixture was exploded. The product, after cooling, was 82 ml, out of which 58 ml were unused oxygen. Show that these results illustrate Gay Lussac's law of gaseous volume.

37. How does the present-day atom differ from Daltonian atom ?

38. Distinguish between the atomic weight, Gram atomic weight and weight of an atom.

39. What is the utility of Atomic mass unit ? Distinguish between the physical and the chemical atomic weights of an element. (*W.B. Joint Ent. 1990*)

40. Calculate the weight of 1 atom of magnesium (Mg=24). [*Ans.* 3·98×10^{-23} g] (*W.B.H.S. 1984*)

41. A compound X_2O_5 is formed by combination of 8·241 g of X with 4·09 g of oxygen. What is the atomic weight of X ? [*Ans.* 80·60]

42. A mixture containing 14 ml of hydrogen and 18·1 ml of chlorine is exploded. If the measurements of the volumes are made at the same temperature and pressure, what is the composition by volume of the resulting mixture ? [*Ans.* HCl=28·0 ml ; Unreacted chlorine=4·1 ml.]

43. (a) What is meant by atomic mass unit ? Calculate the mass of Fluorine atom (F = 19). [*Ans.* 3·154 × 10^{-23}g] [*W.B. J.E. 1990*]

(b) The mass of C^{12} atom is 1·9923 × 10^{-23} g. Find the value of 1 atomic mass unit in gram. [*W.B.H.S. '95*]

44. Copper sulphide contains 33·5% of sulphur. Copper oxide contains 79·9% of copper and sulphur trioxide contains 40·1% of sulphur. Show that these results illustrate the law of reciprocal proportions.

45. Sulphur combines with its own weight of oxygen to produce SO_2. H_2S contains 5·9% of H_2. Water contains 88.89% of O_2. Show that the above results conforms to the law of reciprocal proportions.

46. What are physical atomic weight and chemical atomic weight ? Why physical atomic weight is greater than the chemical atomic weight ? Is there any unit is which atomic weight is expressed ? If so, what is the unit ? (*W.B.J.E.E. 1994*)

47. What is atomic mass unit (a. m. u.) ? The atomic wt. of nitrogen is 14·007 a. m. u. What is the mass of 1 atom of nitrogen in gram ? [*Ans.* 23·24 × 10^{-24}g] [*W.B.H.S. '92*]

48. H_2 gas is passed through one gram of each two heated oxides of *M*, when 0·1258 g and 0·2263 g of water are produced respectively. Show that these data are in conformity with a law of chemical combination. What is the law and who discovered the law ?. [*W.B.H.S. '92*]

49. Do you agree with the statement 'atoms of the same element have same mass while atoms of different elements have different masses'. Explain. [*W.B.J.E. '92*]

50. NH_3 contains 17·65% H_2. Water contains 11·11% H_2 and nitrous oxide contains 36·36% O_2. Show that these data illustrate the law of reciprocal proportions. [*W.B.H.S. '94*]

2

AVOGADRO'S HYPOTHESIS AND MOLECULES

2.1. Introduction to Avogadro's hypothesis.

- **What led to the adoption of Avogadro's hypthesis.**

(i) According to Dalton's atomic theory, during a chemical union, the atoms of different elements combine together in definite numerical proportions, i.e., in a ratio of whole numbers to form the smallest particle of a compound. Dalton's atomic theory did not visualise the concept of the molecule at that juncture.

(ii) Soon after this suggestion of Dalton, Gay Lassac, as a result of a large number of experimental facts concluded that—'Under the same conditions of temperature and pressure, when two or more gases combine together, they do so in simple ratios by volumes, and the volumes of the products if gaseous, also bear a simple relation to the volumes of the reacting gases.

(iii) Berzelius (1808) tried to establish a relationship between the volumes of gases and the number of reacting atoms. Thus in order to correlate Dalton's atomic theory with Gay Lussac's law of gaseous volumes, Berzelius proposed that—*under the same conditions of temperature and pressure equal volumes of all gases contain the same number of atoms.*

(iv) *Defects of Berzelius' hypothesis*—Experimentally it has been observed that under the similar conditions of temperature and pressure one volume of hydrogen combines with one volume of chlorine to produce two volumes of hydrogen chloride.

$$H_2+Cl_2=2HCl$$

Let '*n*' be the number of atoms present in one volume of each of the reacting gases and the product. Then according to Berzelius' hypothesis—*n* atoms of hydrogen combine with *n* atoms of chlorine to produce 2*n* atoms of hydrogen chloride.

or, 1 atom of hydrogen combines with 1 atom of chlorine to produce 2 atoms of hydrogen chloride.

or, $\frac{1}{2}$ atom of hydrogen combines with $\frac{1}{2}$ atom of chlorine to produce 1 atom of hydrogen chloride.

Thus it goes to accept that 1 atom of hydrogen chloride contains $\frac{1}{2}$ atom of hydrogen and $\frac{1}{2}$ atom of chlorine. If that be the case, then each atom of hydrogen and chlorine has to be divided to produce 1 atom of hydrogen chloride. Thus according to Berzelius' hypothesis atoms are divisible. But according to Dalton's atomic theory atoms are indivisible. Thus the hypothesis of Berzelius goes against Dalton's atomic theory and so it was totally rejected.

(v) *Concept of molecule :* In order to overcome this difficulty Italian scientist **Amedeo Avogadro** (1811) put forward his *molecular theory* wherein a clear distinction was made between an atom and a molecule. The word '*atom*' was used by Dalton to describe the smallest particle of either element or compound. The idea of molecule was not known before that time. According to molecular theory. (a) *a molecule is the ultimate particle of a substance (element or compound) which can exist* *in free state and possesses all the characteristic properties of the substance* ; (b) an atom is the ultimate particle of an element which can take part in a chemical reaction. Atoms of gaseous elements can not exist in free state. The gaseous elements contain 2 similar atoms in a combined fashion, whereas in a compound the atoms of different elements exist in a combined way.

Thus all elements and compounds are composed of molecules. The atoms combine together to form molecules, which exist in free state. According to Avogadro, a molecule can be further divided into its constituent atoms which are indivisible during a chemical reaction.

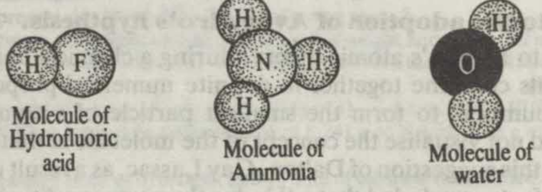


Fig. 2.1

Consequently from the concept of molecule it is clear that a gas always contains molecules as its ultimate particles and hence the volume of a gas must be related to the number of molecules present in it. Thus by modifying Berzelius' hypothesis Avogadro presented a new hypothesis.

- **Avogadro's hypothesis :** *Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.*

According to this hypothesis under the similar conditions of temperature and pressure the number of molecules present in 1 ml of any gas will be the same, whatever be the nature of the gas—whether oxygen or chlorine or CO_2. Thus if *n* number of oxygen molecules are present in 1 litre of the gas under the given conditions of temperature and pressure, then according to Avogadro's hypothesis 1 litre of Cl_2 or 1 litre of CO_2 or 1 litre of NH_3 will contain *n* number of molecules of the respective gases under the identical conditions of temperature and pressure.

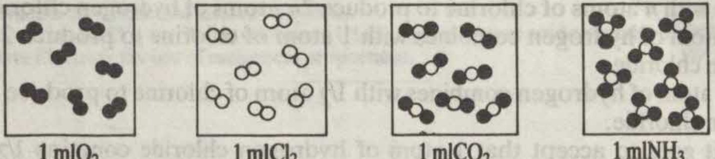


Fig. 2.2

It is to be clearly borne in mind that *the hypothesis never states that the volumes (diameter) of different molecules of different gases are identical.* On the contrary it emphasises that those volumes occupied by the gases are identical where the same number of molecules of the respective gases are present. In fact, the volumes (diameters) of individual molecules of different gases are different.

• How does Avogadro's hypothesis reconcile Gay Lussac's law of gaseous volumes with Dalton's atomic theory ?

Experimentally it has been observed that under the identical conditions of temperature and pressure one volume of hydrogen combines with one volume of chlorine to produce two volumes of hydrogen chloride. Let '*n*' be the number of molecules present in one volume of each of the reacting gases and product. Then according to Avogadro's hypothesis *n* molelcules of hydrogen combine with *n* molecules of chlorine to produce 2*n* molecules of hydrogen chloride.

$$H_2+Cl_2=2HCl$$

or, 1 molecule of hydrogen combines with 1 molecule of chlorine to produce 2 molecules of hydrogen chloride.

or, $\frac{1}{2}$ molecule of hydrogen combines with $\frac{1}{2}$ molecule of chlorine to produce 1 molecule of hydrogen chloride.

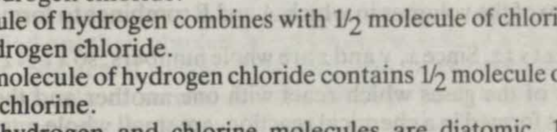
That is, one molecule of hydrogen chloride contains $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine.

Since, both hydrogen and chlorine molecules are diatomic, $\frac{1}{2}$ molecule of hydrogen = 1 atom of hydrogen and $\frac{1}{2}$ molecule of chlorine = 1 atom of chlorine.

That is to say that 1 molecule of hydrogen chloride contains 1 atom of hydrogen and 1 atom of chlorine. This statement does not go against Dalton's atomic theory for the fact that although atoms are indivisible, molecules are divisible. Thus Avogadro's hypothesis reconciled Gay Lussac's law with Dalton's atomic theory.

According to Avogadro's hypothesis melocules are composed of atoms and the molecules are divisible. Consequently during a chemical reaction molecules of the reacting gases split up into their constituent atoms which then unite in simple numerical proportions to form new molecules. The following diagrams illustrate it.

(i) Under the identical conditions of temperature and pressure 1 volume of hydrogen combines 1 volume of chlorine to produce 2 volumes of hydrogen chloride.



1 atom Hydrogen = ○ 1 atom Chlorine = ● 1 molecule Hydrogen = ○○
1 molecule Chlorine = ●● 1 molecule Hydrogen Chloride = ○●

Fig. 2.3

(ii) Under the similar conditions of temperature and pressure 1 volume of nitrogen combines with 3 volumes of hydrogen to produce 2 volumes of ammonia.

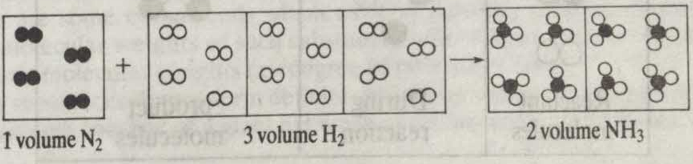


Fig. 2.4

• To prove the law of gaseous volumes with the help of Avogadro's hypothesis.

Gay Lussac's law of gaseous volume can be proved by the application of Avogadro's hypothesis. Let two gases *A* and *B* react together to form another gas *C* under the same conditions of temperature and pressure. Let us suppose x molecules of A combine with y molecules of B to form z molecules of C, where x, y and z are simple whole numbers. According to Avogadro's hypothesis under the similar conditions of temperature and pressure 1 ml of each of A, B and C contains n number of molecules.

Therefore, the volume of x molecules of $A = \frac{x}{n}$ ml,

the volume of y molecules of $B = \frac{y}{n}$ ml,

and the volume of z molecules of $C = \frac{z}{n}$ ml,

Thus, the ratio of the volumes in which A and B combines to form the product C is $\frac{x}{n} : \frac{y}{n} : \frac{z}{n}$ or, $x : y : z$. Since x, y and z are whole numbers, so $x : y : z$ is a simple ratio, or the volumes of the gases which react with one another and the volume of the gaseous product formed in a chemical reaction, are small whole number ratios. This is Gay Lussac's law of gaseous volumes. Thus the law is established on the basis of Avogadro's hypothesis.

2.2. Modification of Dalton's Atomic theory in the light of Avogadro's Molecular Theory.

According to Dalton's Atomic theory, atom is the ultimate particle of both element and compound. Avogadro's hypothesis suggests that although atom is the ultimate particle of element, for compound molecule is the ultimate particle—not atom.

Inert gases and the metals are monoatomic. Hence in their case the term 'atom' is synonymously used for molecule. Since all compounds consist more than one atom of different elements, the ultimate particle of a compound which can exist in the free state is molecule and not atom. Thus, with the adoption of Avogadro's hypothesis a clear distinction can be made between atom and molecule and consequently Dalton's atomic theory has been modified.

(i) All substances—elements or compounds consist of molecules. Molecules are the ultimate particles which can exist in the free state.

(ii) Molecules are composed of atoms which are the ultimate particles of elements.

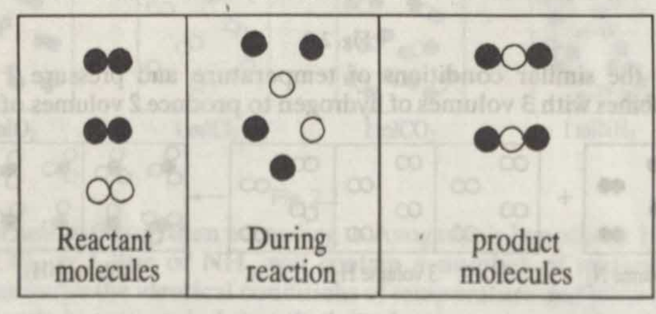


Fig. 2.5

(iii) Molecules are of two types—*Elemental molecules* which consist of atoms of the same element e.g., H_2, N_2, O_2 etc., and *compound molecules* which consist of atoms of different elements e.g. CO_2, H_2SO_4, HNO_3 etc.

(iv) The properties of a substance are, in fact, the properties of its molecules. Molecules of a particular substance are identical in mass and properties while molecules of different substances are different in all respects.

(v) Atoms only can take part in chemical reactions. Molecules are formed by the union of atoms in simple numerical proportions e.g., HCl (1 : 1), NH_3 (1 : 3), H_2SO_4 (2 : 1 : 4) etc.

(vi) During a chemical reaction, the molecules of each substance are first split up into atoms which then unite together in a definite proportion to form new molecules of the new substance or substances e.g., $2H_2 + O_2 = 2H_2O$

2.3. Concept of Molecular Weight.

Like atoms, the molecules are so minute and their weights are so negligible that it is not possible to find out their absolute weight with the help of a chemical balance by direct weighing. The actual weight of one molecule of hydrogen is $3{\cdot}32 \times 10^{-24}$ g and that of one molecule of sucrose is $5{\cdot}68 \times 10^{-22}$ g. Such negligible quantities cannot be used in chemical calculations. To overcome these difficulties comparative values for the weights of molecules are used instead of their actual weights. Hence is the necessity of expressing molecular weights (mass) as their relative weights with reference to a standard atom. Consequently the molecular weights are only numbers and have no unit. Thus,

(i) **Hydrogen scale :** *The molecular weight of an element or a compound is a number which represents how many times a molecule of the element or compound is heavier than one atom of hydrogen.*

$$\text{Molecular weight} = \frac{\text{weight of one molecule of the substance}}{\text{weight of one atom of hydrogen}}$$

(ii) **Oxygen scale :** *The molecular weight of a substance (element or compound) is a number which represents how many times a molecule of the substance is heavier than $^1/_{16}$th part of the weight of an oxygen atom.*

$$\text{Molecular weight} = \frac{\text{weight of 1 molecule of the substance}}{\text{1/16th part of the weight of an atom of oxygen}}$$

(iii) **Carbon scale :** *The molecular weight of a substance (element or compound) is defined as the ratio of the weight of one molecule of the substance to $^1/_{12}$th part of the weight of one atom of C-12 isotope.*

$$\text{Molecular weight} = \frac{\text{weight of 1 molecule of the substance}}{\text{1/12th part of the weight of an atom of C-12 isotope}}$$

(i) The molecular weight of a compound represents the sum of the atomic weights of all atoms shown in the formula of the substance.

(ii) There are some compounds which exist in dimeric, trimeric or polymeric forms. The molecular weights of such substances will be twice, thrice or x times of the monomeric molecular weights (x=degree of polymerisation).

(iii) Many substances do not form definite molecular entities (macro molecules). Silica, for example consists of a giant net work of silicon and oxygen atoms bonded together in a regular manner existing as three dimensional $(-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{O}}-\overset{|}{\underset{|}{Si}}-)$ unit.

(iv) There are some ionic compounds which do not contain discrete molecules e.g., sodium chloride molecules are made up of a regular assembly of Na^+ and Cl^- ions in a crystal lattice. Since this type of ionic specis does not contain any discrete molecule, it is convenient to use the term *'Formula weight'* instead of molecular weight for them.

- **Atomicity :**

The number of atoms in a molecule of an element is called its atomicity.

(i) Thus the atomicity of inert gases (He, Ne, Ar, Kr etc.) and metals like Li, Na, K, Cu etc. is 1.

(ii) The molecules of some elements contain 2 atoms e.g., (H_2, O_2, N_2, Cl_2 etc.). These are diatomic.

(iii) The ozone molecule contains 3 atoms and so its atomicity is 3.

(iv) Phosphorus molecules (P_4) is tetra atomic.

In general, the molecular weight is always the sum of the atomic weights of the atoms in the molecule. Consequently by knowing the composition of the molecule, the molecular weight can easily be calculated.

Element or compound	Molecular formula	Molecular weight
Hydrogen	H_2—two atoms of hydrogen	$2\times1=2$
Oxygen	O_2—two atoms of oxygen	$2\times16=32$
Carbon di-oxide	CO_2—1 atom of carbon and 2 atoms of oxygen	$12\times1+2\times16=44$
Nitric acid	HNO_3—1 atom of hydrogen, 1 atom of nitrogen and 3 atoms of oxygen	$1\times1+14\times1+3\times16=63$
Sulphuric acid	H_2SO_4—2 atoms of hydrogen 1 atom of sulphur and 4 atoms of oxygen	$2\times1+1\times32+4\times16=98$
Glucose	$C_6H_{12}O_6$—6 atoms of carbon, 12 atoms of hydrogen and 6 atoms of oxygen	$6\times12+1\times12+6\times16=180$

2.4. Gram molecule or Gram molecular weight or Gram mole.

The gram-molecular weight of a substance (element or compound) is simply the molecular weight of the substance expressed in grams. It is more commonly known as **gram molecule** or **gram mole** or **mole.**

In other words, *gram molecular weight of an element or compound is that weight in gram which contains the same number of molecules as the number of atoms contained in 12 gram of carbon 12.*

The molecular weights of oxygen and hydrogen are 32 and 2 respectively. Thus 32 g of oxygen represent 1 gram molecular weight of oxygen or 1 gram mole of oxygen, 64 g (2×32) of oxygen represent 2 gram moles of O_2 and 6 g (3×2) of H_2 represent 3 gram moles of hydrogen. Molecular weight of H_2SO_4 is 98, so 98 g of H_2SO_4 represent 1 gram mole of H_2SO_4 and 49 g of H_2SO_4 represent 0·5 mole of H_2SO_4.

Thus, *the gram molecular weight of a substance represents a definite weight of that substance which is equal to its molecular weight expressed in gram.*

2.5. Gram molecular volume or molar volume.

The volume occupied by one gram molecular weight of any gas or vapour (element or compound) at a fixed temperature and pressure is known as molar volume of that gas or vapour at that temperature and pressure.

From Avogadro's hypothesis it has been proved that 1 gram mole of any gas or vapour occupies 22·4 litre at N.T.P.

The volume occupied by 1 gram molecule of any gas (element or compound) at N.T.P. is known as the molar volume of that gas at N.T.P. This volume does not depend on the nature of the gas.

Thus 1 gram mole of H_2=2 g of H_2, 1 gram mole of CO_2=44 g of CO_2, 1 gram mole of NH_3=17 g of NH_3

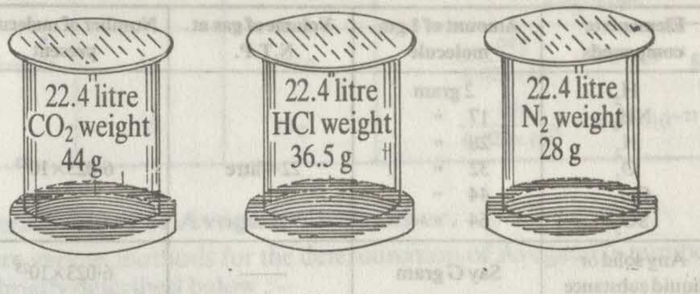


Fig. 2.6

Now at normal conditions of temperature and pressure (N.T.P.) the volume of 2 g of H_2 or 44 g of CO_2 or 17 g of NH_3 will be 22·4 litre. Similarly 2 gram moles of any gas will occupy 2×22·4 litre.

Again, 22·4 litre of any gas is the volume of one gram mole of that gas at N.T.P. and one gram mole of any substance contains $6{\cdot}023\times10^{23}$ (Avogadro's number) molecules. Hence $6{\cdot}023\times10^{23}$ molecules of any substance in the vapour or gaseous state will weigh 1 gram molecular weight of that substance and occupy 22·4 litre at N.T.P.

The gram molecular weights and their volumes at N.T.P. of some gaseous substances are given below.

Substance	Molecular weight	Gram molecular weight	Gram-mole	Weight in gm	Volume at N.T.P.
CO_2	44	44 gram	1	44 gram	22·4 litre
CO	28	28 "	2	56 "	44·8 "
SO_2	64	64 "	1	64 "	22·4 "
H_2S	34	34 "	4	136 "	89·6 "
Cl_2	71	71 "	1	71 "	22·4 "
N_2	28	28 "	3	84 "	67·2 "
O_2	32	32 "	5	160 "	112 "
H_2	2	2 "	10	20 "	224 "

2.6. Avogadro's Number.

According to Avogadro's hypothesis under the same conditions of temperature and pressure equal volumes of all gases contain the same number of molecules. Again we know one mole or one gram mole of any gas or vapour occupies 22·4 litre at N.T.P. Hence it can be concluded that one gram mole of any substance contains the same number of molecules although the weights of the molecules are quite different.

The number of particles present in one mole of a substance (element or compound) is known as **Avogadro's number.** *It is equal to* $6{\cdot}023\times10^{23}$. Avogadro number is represented as *'N'*. Thus, in one gram molecule of any substance (element or compound) the total number of molecules is $6{\cdot}023\times10^{23}$ and in one gram atom of any element the number of atoms present is $6{\cdot}023\times10^{23}$.

Since one gram molecule or one gram mole of any gas occupies 22·4 litre at N.T.P. *Avogradro's number may also be defined as the total number of molecules present in 22·4 litre of any gas at N.T.P.*

The following table illustrates the relation among gram molecular weight or gram mole, molar volumes at N.T.P. and the Avogadro's number.

Elements or compounds	Amount of 1 gm molecule	Volume of gas at N.T.P.	Number of molecules present
H_2	2 gram	22·4 litre	$6{\cdot}023\times10^{23}$
NH_3	17 "		
N_2	28 "		
O_2	32 "		
CO_2	44 "		
SO_2	64 "		
Any solid or liquid substance	Say G gram	——	$6{\cdot}023\times10^{23}$

The following table indicates the number of atoms present per gram atom of any element.

Elements	Amount of 1 gram atom	Number of atoms present
O	16 gram	$6{\cdot}023\times10^{23}$
C	12 "	
Br	80 "	
Mg	24 "	

- **To find out the actual weight of an atom or a molecule with the help of Avogadro's number.**

One gram mole of an element or compound contains $6{\cdot}023\times10^{23}$ molecules. Therefore the total weight of all these molecules is its gram molecular weight. In other words *the gram molecular weight of an element or compound is the weight of its* $6{\cdot}023\times10^{23}$ *(Avogadro's number) molecules taken together, the unit being gram.*

Hence by dividing the gram molecular weight of a substance by $6{\cdot}023\times10^{23}$, the actual weight of a molecule or an atom of the substance can be found out.

Thus, 1 gram molecule of hydrogen = 2 g

$$\therefore \text{ the weight of 1 molecule of hydrogen} = \frac{2\text{ g}}{6{\cdot}023\times10^{23}} = 3{\cdot}34\times10^{-24}\text{ g}$$

$$\text{weight of 1 atom of hydrogen} = \frac{3{\cdot}34\times10^{-24}}{2} = 1{\cdot}67\times10^{-24}\text{ g}$$

(since hydrogen molecule is diatomic)

Actual weights of some molecules are tabulated below :—

Molecule	Molecular weight	Gram molecular weight	Actual weight of a molecule = $\frac{\text{gram molecular weight}}{6{\cdot}023\times10^{23}}$
Oxygen	32	32 g	$\frac{32\text{ g}}{6{\cdot}023\times10^{23}} = 5{\cdot}31\times10^{-23}\text{ g}$
Nitrogen	28	28 g	$\frac{28\text{ g}}{6{\cdot}023\times10^{23}} = 4{\cdot}64\times10^{-23}\text{ g}$

Molecule	**Molecular weight**	**Gram molecular weight**	**Actual weight of a molecule =** $\frac{\textbf{gram molecular weight}}{\mathbf{6{\cdot}023\times10^{23}}}$
Carbon-di-oxide	44	44 g	$\frac{44\text{ g}}{6{\cdot}023\times10^{23}} = 7{\cdot}3\times10^{-23}\text{ g}$
Water	18	18 g	$\frac{18\text{ g}}{6{\cdot}023\times10^{23}} = 2{\cdot}99\times10^{-23}\text{ g}$

• Determination of Avogadro's Number.

There are various methods for the determination of Avogadro's number. Two of these are briefly described below :—

(i) *Millikan's oil drop experiment :* In 1913 Millikan by his 'oil drop experiment' determined the charge of an electron. In his experiment the movement of an oil drop in an electric field was observed. Now the velocity of the moving oil drop was related to the charge which it carried. From this relation the charge carried by a single oil drop was found to be $1{\cdot}6\times10^{-19}$ coulomb. This quantity of charge was proved to be the charge of an electron. Since the charge carried by one mole of electron = 1 Faraday = 96500 coulomb, the value of $N = \frac{96500}{1{\cdot}6\times10^{-19}} = 6{\cdot}03\times10^{23}$

(ii) *From measurements on radio-active substance :* Rutherford observed that $11{\cdot}6\times10^{17}$ alpha particles were emitted from 1 gram of Ra in one year. Each of the emitted alpha particle (He^{++}) accepts electrons from the atmosphere to form a He atom. Again $7{\cdot}66\times10^{-6}$ g of helium is formed from 1 gram of Ra in one year.

Now if $7{\cdot}66\times10^{-6}$ g of He is made up of $11{\cdot}6\times10^{17}$ alpha particles, then 4 g of He or 1 mole of He contains :—

$$\frac{11{\cdot}6\times10^{17}\times4}{7{\cdot}66\times10^{-6}} \approx 6{\cdot}06\times10^{23} \text{ molecules or, Avogadro's number} = 6{\cdot}06\times10^{23}$$

The present accepted value of Avogadro's number $N = 6{\cdot}023\times10^{23}$

2.7. Applications of Avogadro's hypothesis and its important deductions.

Avogadro's hypothesis has led to the following important deductions and applications in chemistry.

(i) *Determination of the atomicity of elementary gases.*

(ii) *Deduction of the relationship between the molecular weight of a gas and its vapour density.*

(iii) *Determination of the molecular formula of a gas from its volumetric composition.*

(iv) *Determination of atomic weights of elements.*

(v) *Determination of the molecular weights of gaseous or volatile substances.*

(vi) *Establishment of the fact that the gram molecular volume of any gaseous substance occupies 22·4 litre at N.T.P.*

(1) The molecules of elementary gases (except inert gases) are diatomic.

Actual experiments have shown that under the same conditions of temperature and pressure 1 volume of H_2 combines with 1 volume of Cl_2 to yield 2 volumes of hydrogen chloride.

Let n be the number of molecules present in 1 volume of each gas taking part in the reaction. Now substituting volumes by number of molecules (from Avogadro's law) we get,

n molecules of hydrogen + n molecules of chlorine = $2n$ molecules of hydrogen chloride.

Or, 1 molecule of hydrogen + 1 molecule of chlorine = 2 molecules of hydrogen chloride.

Or, $1/2$ molecule of hydrogen + $1/2$ molecule of chlorine = 1 molecule of hydrogen chloride.

Since atom is the ultimate particle of matter, the molecule of any element must contain atleast one atom, not a fraction of it.

Again, since hydrogen chloride is a compound of only hydrogen and chlorine, the compound must contain atleast 1 atom of hydrogen and 1 atom of chlorine. This 1 atom of each element must definitely comes from $1/2$ molecule of hydrogen and $1/2$ molecule of chlorine. Thus $1/2$ molecule of hydrogen and $1/2$ molecule of chlorine contain 1 atom of hydrogen and 1 atom of chlorine respectively. Consequently 1 molecule of hydrogen and 1 molecule of chlorine must contain at least two atoms each, i.e., a molecule of hydrogen or chlorine is diatomic.

This can further be confirmed by the following reasonings—

Since hydrogen present in the hydrochloric acid can be replaced by a metal like sodium yielding one and only one normal salt e.g., NaCl, we are to believe that 1 molecule of hydrochloric acid contains only one replacable hydrogen atom. But it has already been proved that hydrochloric acid contains $1/2$ molecule of hydrogen.

$\therefore$ $1/2$ molecule of hydrogen = 1 atom of hydrogen.

or, 1 molecule of hydrogen = 2 atoms of hydrogen.

In like manner, it may be proved that a molecule of any elementary gas like fluorine, oxygen, nitrogen etc., is also diatomic.

[It has been found out experimentally that for an elementary gas having diatomic molecules, the ratio of specific heat at constant pressure (C_p) to the specific heat at constant volume (C_v) is nearly constant and lies between 1·4 and 1·41. The ratio C_p/C_v for hydrogen, oxygen and chlorine is found to be 1·41, 1·4 and 1·4 respectively. This agreement strongly proves that the elementary gases except the insert gases, are diatomic. For mono atomic gases this value is 1·61.]

(2) Relation between molecular weight, normal density and vapour density of a gas.

- **Normal density :** *The normal density of a gas is defined as the weight in gram of 1 litre of the gas at N.T.P.*

The normal density of oxygen is 1·43 g/lit—means that the weight of 1 litre of oxygen at N.T.P. is 1·43 g.

$$\text{Normal density} = \frac{\text{weight of the gas in gram}}{\text{volume of the gas in litre at N.T.P.}}$$

Normal density depends on temperature and pressure.

- **Vapour density or relative density :**

Vapour density of a gas or vapour is the ratio of the weight of a given volume of gas (or vapour) to the weight of an equal volume of hydrogen, both measured under the same conditions of temperature and pressure.

So, vapour density does not depend on temperature and pressure.

'The vapour density of SO_2 is 32'— means that under the same conditions of temperature and pressure, certain volume of SO_2 is 32 times heavier than the same volume of hydrogen.

• Relation between normal density and vapour density :

From the definition we get,

$$\text{Vapour density of gas} = \frac{\text{weight of } V \text{ litre of the gas at N.T.P.}}{\text{weight of } V \text{ litre of hydrogen at N.T.P.}}$$

$$= \frac{\text{weight of 1 litre of the gas at N.T.P}}{\text{weight of 1 litre of hydrogen at N.T.P.}}$$

$$= \frac{\text{normal density of the gas}}{\text{normal density of hydrogen}}$$

Or, under the same conditions of temperature and pressure, the normal density of any gas = Its vapour density × normal density of hydrogen.

Now, the normal density of hydrogen = weight of 1 litre of hydrogen at N.T.P. = 0·089 g.

Or, *at N.T.P. the normal density of any gas = Its vapour density × 0·089*

Thus, while the *normal density or density of a gas or vapour is expressed in g/litre, while its vapour density has no unit—it is a pure number.*

• Relation between molecular weight and vapour density of a gas :

This important relationship was derived by Cannizzaro by a straight forward application of Avogadro's hypothesis.

We know that the,

$$\text{Vapour density } (V.D) \text{ of a gas} = \frac{\text{weight of a certain volume of the gas or vapour}}{\text{weight of an equal volume of hydrogen}}$$

(both measured under the same conditions of temperature and pressure)

$$= \frac{\text{weight of } V \text{ volume of the gas or vapour}}{\text{weight of } V \text{ volume of hydrogen}}$$

Let n be the number of molecules present per V volume of gas. Applying Avogadro's hypothesis—

$$V.D. = \frac{\text{weight of } n \text{ molecules of the gas or vapour}}{\text{weight of } n \text{ molecules of hydrogen}}$$

$$= \frac{n \times \text{weight of 1 molecule of the gas or vapour}}{n \times \text{weight of 1 molecule of hydrogen}}$$

$$= \frac{\text{weight of 1 molecule of the gas or vapour}}{\text{weight of 1 molecule of hydrogen}}$$

Since hydrogen molecule is diatomic, the weight of 1 molecule of hydrogen must be twice the weight of 1 atom of hydrogen. It follows therefore :

$$V.D. = \frac{\text{weight of 1 molecule of the gas or vapour}}{2 \times \text{weight of 1 atom of hydrogen}}$$

[Since the molecular weight of any compound or element, (solid, liquid or gas)

$$= \frac{\text{weight of 1 molecule of the element or compound}}{\text{weight of 1 atom of hydrogen}}]$$

$$V.D. = \frac{\text{Molecular weight of the gas or vapour}}{2}$$

or, **molecular weight = *2 × V.D.***

[The correct atomic weight of hydrogen on C^{12} scale is 1·008.

For an accurate result, the relation will be, *molecular weight = 2·016 × V.D.*

However, the simple relation that the molecular weight of any gas or vapour is twice its vapour density is more frequently used and in this book we shall always refer to this.]

Since vapour density of gases can be easily found out by accurate experiments, this relation enables us to find the molecular weights of gases.

(3) **Determination of molecular formula of a gas from its volumetric composition.**

The molecular formula of a gaseous compound can be easily worked out from a knowledge of its vapour density and its composition by volume. We shall now proceed to determine the molecular formula of 3 gases with the help of Avogadro's hypothesis.

(a) **Molecular formula of hydrogen chloride :**

By actual experiments it is found that 1 volume of hydrogen combines with 1 volume of chlorine to form 2 vols of hydrogen chloride, under the same conditions of temperature and pressure.

Let n be the number of molecules present in 1 vol of hydrogen or chlorine.

$\therefore$ n molecules of hydrogen combine with n molecules of chlorine to form $2n$ molecules of hydrogen chloride.

or, 1 molecule of hydrogen combines with 1 molecule of chlorine to form 2 molecules of hydrogen chloride.

or, $1/2$ molecule of hydrogen combines with $1/2$ molecule of chlorine to form 1 molecule of hydrogen chloride.

Since both hydrogen and chlorine are diatomic, $1/2$ molecule will contain 1 atom each.

Thus, 1 molecule of hydrogen chloride contains 1 atom of hydrogen and 1 atom of chlorine.

So the emperical formula of hydrogen chloride is HCl. By actual experiment it is found that the vapour density of HCl = 18·25

$\therefore$ Mol wt. of HCl = $2 \times 18{\cdot}25 = 36{\cdot}5$

Let the molecular formula of hydrogen chloride be $(\text{HCl})_x$

or, $(\text{HCl})_x = 36{\cdot}5$

or, $(1 + 35{\cdot}5)_x = 36{\cdot}5$

or, $36{\cdot}5x = 36{\cdot}5$

or, $x = 1$

Hence the molecular formula of hydrogen chloride is HCl.

(b) **Molecular formula of ammonia :**

Volumetric analysis shows that under the same conditions of temperature and pressure 3 vols of hydrogen combine with 1 vol of nitrogen to form 2 vols of ammonia.

Let n be the number of molecules present per volume of each gas, then according to Avogadro's hypothesis,

$3n$ molecules of hydrogen + n molecules of nitrogen = $2n$ molecules of ammonia.

or, 3 molecules of hydrogen + 1 molecule of nitrogen = 2 molecules of ammonia.

or, 6 atoms of hydrogen + 2 atoms of nitrogen = 2 molecules of ammonia.

[$\because$ both nitrogen and hydrogen molecules are diatomic]

or, 1 molecule of ammonia contains 3 atoms of hydrogen and 1 atom of nitrogen.

Hence the emperical formula of ammonia is NH_3.

By actual experiment it is found that the vapour density of ammonia is 8·5

$\therefore$ Molecular wt. of ammonia is $8{\cdot}5 \times 2 = 17$.

Let the molecular formula of ammonia be $(NH_3)_x$ (where x is a whole number)

or, $(14 + 3)_x = 17$

or, $17x = 17$

or, $x = 1$

Hence the molecular formula of ammonia is NH_3.

(c) Molecular formula of nitrous oxide :

By actual experiment it is observed that nitrous oxide is a compound of nitrogen and oxygen and it contains its own volume of nitrogen.

Let n be the number of molecules present in 1 vol of nitrous oxide.

According to Avogadro's hypothesis,

n molecules of nitrous oxide contain n molecules of nitrogen.

or, 1 molecule of nitrous oxide contains 1 molecule of nitrogen.

Hence the emperical formula of nitrous oxide is N_2O_x where $x =$ the number of oxygen atoms present in 1 molecule of nitrous oxide.

From actual experiment it is found that the vapour density of nitrous oxide = 22

Hence mol. wt. of nitrous oxide = 2 × 22 = 44. The molecular weight of nitrous oxide as calculated from its emperical formula $= 2 \times 14 + x \times 16 = 28 + 16x$

$\therefore\ 28 + 16x = 44$

$16x = 44 - 28 = 16$

or, $x = 1$

Hence the molecular formula of nitrous oxide is N_2O.

(4) Determination of atomic weight of an element—Cannizzaro's method :

Determination of atomic weights of elements with the help of Avogadro's hypothesis can be successfully applied in the case of gaseous elements by the knowledge of vapour density of these elements or some of their volatile compounds.

(i) In this method the vapour density of the gaseous element is determined accurately. Applying the formula Mol. wt.$=2\times V.D.$, the molecular weight of the gas is ascertained. Then by dividing the molecular weight with the atomicity of the molecule, the atomic weight of the gaseous element can be easily found out.

$$\text{Atomic weight} = \frac{2\times V.D.}{\text{Atomicity}} = \frac{\text{Molecular weight}}{\text{Atomicity}}$$

Example : By actual experiment the vapour density of nitrogen has been found to be 14. Hence its molecular weight $=2\times 14=28$.

As the molecule of nitrogen is diatomic according to Avogadro's hypothesis,

$$\text{The atomic weight of nitrogen} = \frac{28}{2} = 14.$$

(ii) *Cannizzaro's method :*

One of the methods for finding the atomic weight of gaseous elements or elements which form gaseous compounds is due to Cannizzaro. The atomic weights of some important elements like carbon, nitrogen, oxygen etc. could not be found either by Dulong and Petit's method or by applying the law of isomorphism. In these cases Cannizzaro's method can be successfully applied to find out the atomic weights of these elements as they form a large number of gaseous or volatile compounds.

Principle : An element may combine with other elements to form a series of volatile gaseous compounds. The molecular weights of each may be obtained from a knowledge of their vapour densities. The molecule of these different compounds may contain 1, 2 or more atoms of the element. Since according to Dalton's atomic theory, atoms are indivisible, only 1 atom of the element *must* be present atleast in 1 compound of the large number of compounds which the particular element forms. Cannizzarro suggested that the *smallest weight of an element present in 1 mole of any of its compounds, is its atomic weight.* In this way he approached the idea of atomic weight in a different way from that adopted by his predecessors.

Procedure : In short, Cannizzarro's method for the determination of atomic weight of an element involves the following steps.

(a) Some volatile gaseous compounds of the element whose atomic weight is to be determined are prepared in the pure state.

(b) The vapour densities of these compounds are found out accurately by actual experiments.

(c) The molecular weights of these compounds are calculated from the relation, *Mol. wt.* $=2\times$ *vapour density.*

(d) The compounds are then analysed to find the percentage by weight of the element present in each compound.

(e) From the molecular weight and percentage composition, the weight of the element present in 1 mole of each of the compound is next found out by applying the following formula.

$$\textit{Wt. of the element in 1 mole} = \frac{\textit{Mol. wt. of the compound} \times \textit{percentage of the element in that compound}}{100}$$

(f) The smallest weight of the element found in 1 mole of any of these compounds is then determined. This smallest or the least weight will be the atomic weight of the element *on the assumption that at least in some of the compounds of the element, only 1 atom of it is present per mole or only 1 gm-atom per mole.*

The application of this method is illustrated to find the atomic weight of *carbon*.

Atomic Weight of Carbon :

Different gaseous compounds of carbon	Vapour density (H=1)	Mol. wt. M =2×V.D	1 mole	% by wt. of carbon in the compound	Weight of carbon in 1 mole (in gram)
Methane	8	16	16 g	75·0	$\frac{75\cdot0\times16}{100}=12$
Ethane	15	30	30 g	80·0	$\frac{80\times30}{100}=24$
Acetylene	13	26	26 g	92·3	$\frac{92\cdot3\times26}{100}=24$
Carbon monoxide	14	28	28 g	42·9	$\frac{42\cdot9\times28}{100}=12$
Carbon di oxide	22	44	44 g	27·3	$\frac{27\cdot3\times44}{100}=12$
Benzene	39	78	78 g	92·3	$\frac{92\cdot3\times78}{100}=72$
Ethylene	14	28	28 g	85·7	$\frac{85\cdot7\times28}{100}=24$

Since the smallest weight of carbon in 1 mole of any carbon compound is 12 g, the atomic weight of carbon, according to Cannizzarro's method, is 12.

- **Limitations of Cannizzaro's method :**

(i) This method is applicable to those elements which can form a large number of volatile or gaseous compounds. Metallic elements normally do not form volatile or gaseous compounds. Hence the atomic weight of metals cannot be determined by this method.

(ii) The Atomic weight values obtained in this way are not accurate because the relation, Mol. wt. $=2\times$V.D. is only accurate for perfect gas.

(iii) This method is not applicable to those vapours or gases which undergo dissociation or association in the vapour state, as the vapour densities of these gases determined on the basis of formula may not be correct.

(iv) The very assumption that "out of a large number of a volatile or gaseous compounds of the elements atleast one compound contains a single atom of the element in its molecules" is not universal. In those cases the calculated atomic weight may be some multiples of the true atomic weight.

(v) This method of finding the atomic weight takes much time and the procedure of this method is laborious.

In spite of the above limitations, Cannizzaro was successful in determining the atomic weights of hydrogen, carbon, silicon, nitrogen, oxygen, phosphorous, arsenic, sulphur, chlorine, bromine and iodine. Moreover his method was the first to indicate the number of atoms present in one molecule of various compounds which Dalton and early workers had not been able to predict.

(5) **The Molar volume of all gases is the same under identical conditions of temperature and pressure and its value is 22·4 litre at N.T.P.**

On the basis of Avogadro's hypothesis, it can be accurately shown that the number of molecules present in one gram molecule of any substance (element or compound) is the same.

Let the molecular weight of the substance be M and the weight of 1 atom of hydrogen be x g.

$\therefore$ wt. of 1 gram mole of the substance $= M$ g.

We know,

$$\text{Mol. wt.} = \frac{\text{weight of 1 molecule of the substance}}{\text{weight of 1 atom of hydrogen}}$$

$$M = \frac{\text{weight of 1 molecule of the substance}}{x\text{ g}}$$

or, weight of 1 molecule of the substance $= xM$ g.

Now the weight of 1 gram molecule of the substance $= M$ g

Hence the number of molecule of the substance present in its 1 gram mole $= \dfrac{M}{Mx} = \dfrac{1}{x}$

Since x is the wt. of 1 molecule of hydrogen $\dfrac{1}{x}$ is constant or the number of molecule present per gram mole of any substance is a constant quantity. As for examples in cases of hydrogen and sulphur dioxide—

(a) The atomic wt. of hydrogen = 1

The mol. wt. of hydrogen = 2

Let the absolute wt. of 1 atom of hydrogen be x g

then the true wt. of a molecule of hydrogen is $2x$ g

$\therefore$ The number of hydrogen molecule in 1 gram mole of hydrogen or 2 g hydrogen

$$= \frac{2\text{ g}}{2x\text{ g}} = \frac{1}{x}$$

(b) The vapour density of SO_2 is 32

Hence its mol. wt. $= 2\times32 = 64$ or, 1 gram mole of SO_2 is 64 g. Since the wt. of 1 molecule of SO_2 is 64 times heavier than 1 atom of hydrogen, the wt. of 1 molecule of $SO_2 = 64x$ g.

$\therefore$ The number of SO_2 molecules present in its gram mole $= \frac{64\text{ g}}{64x\text{ g}} = \frac{1}{x}$

Hence in 1 gram molecule of all substances, elementary or compound, the same number of molecules are present.

Thus, (i) one gram mole of any gas contains the same number of molecules which is $6{\cdot}023 \times 10^{23}$. (*Avogadro's number*). (ii) Following Avogadro's hypothesis, the same number of molecules of different gases occupy the same volume measured under the same conditions of temperature and pressure. Thus, the volume of one gram molecule i.e., the molar volume of all substances in the gaseous state is the same. *Hence under the same conditions of temperature and pressure the molar volume of all gases is the same.*

This can be easily deduced from Avogadro's hypothesis as follows :—

Let the vapour density of a gas or vapour be D.

then by definition, $D = \frac{\text{Wt. of 1 litre of any gas at N.T.P.}}{\text{Wt. of 1 litre of hydrogen at N.T.P.}}$

Since wt. of 1 litre of hydrogen at N.T.P. = 0·089 g.

$$D = \frac{\text{Wt. of 1 litre of the gas at N.T.P.}}{0{\cdot}089\text{ g}}$$

or, wt. of 1 litre of a gas at N.T.P. = $(D \times 0{\cdot}089)$ g.

Again from Avogadro's hypothesis,

Mol. wt. = 2 × vapour density.

If M = Mol. wt. of the gas, vapour density $= \frac{M}{2}$

or, weight of 1 litre of any gas at N.T.P. $= \frac{M}{2} \times 0{\cdot}089$ g.

or, Volume of $\left(\frac{M}{2} \times 0{\cdot}089\right)$ gram of any gas at N.T.P. = 1 litre

or, Volume of M g or one gram mole of any gas at N.T.P. $= \frac{2}{0{\cdot}089} = 22{\cdot}27$ litre

Since the true Mol. wt. of hydrogen is 2·016

Hence, Vapour density $= \frac{M}{2{\cdot}016}$

or, volume of 1 gram mole of any gas at N.T.P. $= \frac{2{\cdot}016}{0.089} = 22{\cdot}4$ litre

Thus, *Molar volume i.e., the volume of 1 gram molecule of all gases at N.T.P. is 22·4 litre.*

- **Ratio of the gaseous molecules, when the volumes are same and when the masses are same.**

We know that the volume of 1 gram mole of all gases at N.T.P. is 22·4 litre. Hence despite the differences in the ratio of the molecular weights, under the same conditions of temperature and pressure the ratio of the number of molecules of the same volume of gas will always be 1:1. But this constancy in the number of molecules will not be maintained in the gases having the same masses. Here the ratio of the number of molecules depends upon the ratio of their molecular weights. This can be illustrated by the following two tables :—

Gaseous substances having the same volume but different masses.

Substance	Mol. weight	Gram mole	Vol. at N.T.P.	Number of Molecules	Ratio of the number of Molecules	Ratio of the volume at the same temp. and pressure
O_2	32	1	22·4 lit.	N	N:N = 1:1	22·4:22·4 = 1:1
SO_2	64	1	22·4 lit.	N		

Gaseous substances having the same masses.

Substance	Mass	Gram mole	Vol. at N.T.P.	Number of Molecules	Ratio of the number of Molecules	Ratio of the volume at the same temp. and pressure
O_2	32 g	1	22·4 lit.	N	2:1	2:1
SO_2	32 g	½	11·2 lit.	N/2		

[• **Relation between mol. wt. and normal density :**

Let M be the molecular wt. and d be the normal density in gm lit^{-1} of a gas.
Wt. of 1 litre of the gas at N.T.P. = d g
$\therefore$ The volume of one gm mole of the gas at N.T.P. = $\frac{M}{d}$ litre = 22·4 litre or, $M = 22{\cdot}4\,d$]

2.8. Importance of Avogadro's hypothesis in chemistry.

Avogadro's hypothesis played a significant role in the development of chemistry in the last century. Although the hypothesis cannot be experimentally verified in the laboratory but the conclusions made on the basis of it, were found to agree well with the experimental data. We are not in a position today to contradict the hypothesis with the help of any facts. Hence, Avogadro's hypothesis may be rightly called as *Avogadro's Law*.

The main uses of this hypothesis may be summarised as follows :

(i) It introduces the differences between atoms and molecules, thus giving a clear picture about the structure of matter.

(ii) It leads to Cannizzaro's method of determining atomic weights and molecular formulae.

(iii) Gay Lusaac's law of combining volumes can be properly explained by Avogadro's hypothesis.

(iv) It rectifies Dalton's Atomic theory and firmly puts forward the molecular theory of matter.

(v) Representation of a chemical reaction by a suitable equation was an indirect consequence of this hypothesis.

(vi) It introduces the idea of atomicity of elements.

(vii) It leads to the important relationship Mol. wt. = $2 \times V.D.$ This method is used to find the molecular weights of gaseous compounds from the measurements of vapour density.

(viii) It gives the idea of Avogadro's number which enables us to calculate the number of molecules in x g of a substance of mol. wt. (M). This will be $\frac{6\cdot023\times x}{M}$.

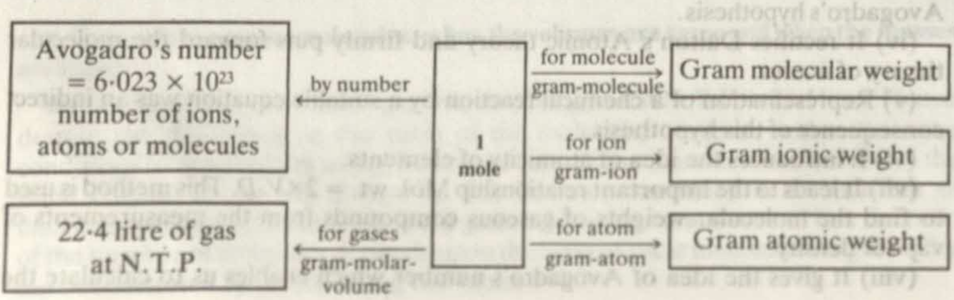
(ix) The ideas of gram molecular weight or mole and molar volume are direct consequences of Avogadro's hypothesis. It further provides the result that 1 mole of any substance contains the same number of molecules and 1 mole of a gas occupies 22·4 litre at N.T.P.

2.9. Concept of Mole.

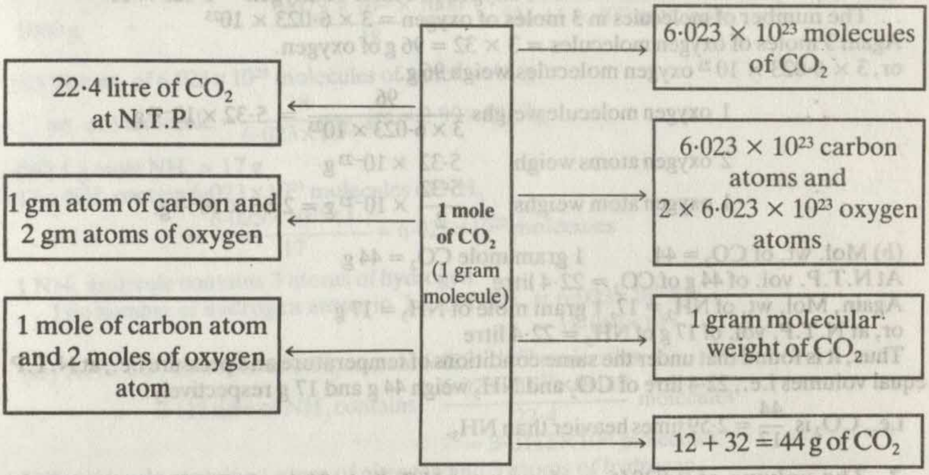
As already mentioned *one gram atom* of any element represents the atomic weight of that element in grams. The atomic weight of nitrogen is 14. Thus 14 g of nitrogen represent 1 gram atom of nitrogen. Similarly, *1 gram mole or gram molecule* represents the molecular weight of the substance expressed in grams. Thus 1 gram molecule of water is 18 g of water. It is evident from Avogadro's hypothesis that *one mole or 1 gram mole of any gas or vapour contains the same number of molecules.* The importance of using the quantity known as *mole* is that it contains the same number of molecules irrespective of the gas or vapour. This number is called *Avogadro's number* which is $6\cdot023\times10^{23}$. Thus, the number of molecules present in 1 gram mole of water i.e., 18 g of water is $6\cdot023\times10^{23}$. Again the gram molecular volume of all gases or vapour at N.T.P. is 22·4 litre. Therefore it can be fairly argued that *the number of molecules present in 22·4 litre of any gas or vapour at N.T.P. is* $6\cdot023\times10^{23}$. Not only molecule, 1 gram atom of any element also contains $6\cdot023\times10^{23}$ atoms of that element or in other words 16 g represent 1 gram atom of oxygen or $6\cdot023\times10^{23}$ atoms of oxygen.

Mole is a unit of counting the number of atoms or molecules present per gram atom or gram molecules of the substance. It also represents the weight of the substance (element or compound) expresses in gram which contains Avogadro number or 6.023×10^{23} *particles (atoms or molecules) of that substance.*

6.023×10^{23} molecules of CO_2 are present in 22.4 litre of CO_2 at N.T.P. Thus the volume 22.4 litre of CO_2 at N.T.P. represents one mole of CO_2. *Like other units e.g., dozen, pair etc.*, used in the daily life, mole is a unit conveniently used by chemists to represent number of particles. Thus, 1 mole electron means $6\cdot023\times10^{23}$ number of electrons. 1 mole of pencil means 6.023×10^{23} number of pencils (a fantastic number !). Hence the meaning of 1 mole may be represented as follows :—



The different meanings of 1 mole of CO_2 are represented by the following diagram.


22·4 litre of CO_2 at N.T.P.
1 gm atom of carbon and 2 gm atoms of oxygen
1 mole of carbon atom and 2 moles of oxygen atom
1 mole of CO_2 (1 gram molecule)
$6{\cdot}023 \times 10^{23}$ molecules of CO_2
$6{\cdot}023 \times 10^{23}$ carbon atoms and $2 \times 6{\cdot}023 \times 10^{23}$ oxygen atoms
1 gram molecular weight of CO_2
$12 + 32 = 44$ g of CO_2

- **Advantage of Mole Concept :**

The mole concept has wide applications in chemistry specially in physical and analytical chemistry. Chemical calculations can be made in a simple and convenient way by observing the fact that there is a relationship between the number of moles of the reactants and products. So instead of calculating the weights of reactants and products, the mole ratio method is more simple and convenient. Thus

$$2CO + O_2 = 2CO_2$$

This equation shows that 56 g of CO combine with 32 g of O_2 to form 88 g of CO_2. Now representing in terms of mole, we can say, 2 moles of CO react with 1 mole of oxygen to form 2 moles of CO_2. Since 1 mole of $CO_2 = 44$ g hence 2 moles of $CO_2 = 2 \times 44 = 88$ g. The weight of CO_2 formed in the above reaction is 88 g. The actual weight of a molecule, an atom, an ion or even the charge of an electron can be evaluated from a knowledge of the mole concept.

It should be clearly remembered that whenever the term *mole* is used, the unit of the particle i.e., molecules, atom or ion *must* always be mentioned e.g.,

1 gram molecule of O_2 = 32 g of O_2 = 1 mole oxygen molecule
1 gram atom of O_2 = 16 g of O_2 = 1 mole oxygen atom
2 gram molecules of Na = 46 g of Na = 2 moles Na-atom
1·25 gram molecules of CO_2 = 55 g of CO_2 = 1·25 moles CO_2 molecule
5 gram atoms of C = 60 g of C = 60/12 = 5 moles C-atoms
1 gram ions of Na = 23 g of Na^+ = 1 mole of Na^+ ions

• WORKED OUT EXAMPLES •

2.10. Problems on Avogadro's hypothesis.

1. (a) *Calculate the number of oxygen molecule in 3 gram molecules of oxygen and express the mass of 1 atom of oxygen in it.*

(b) *Show that under the same conditions of temperature and pressure a certain volume of CO_2 is 2·59 times heavier than the same volume of NH_3.*

Ans : (*a*) The number of molecules of oxygen in 1 mole of oxygen = $6{\cdot}023 \times 10^{23}$

$\therefore$ The number of molecules in 3 moles of oxygen = $3 \times 6{\cdot}023 \times 10^{23}$

Again 3 moles of oxygen molecules = $3 \times 32 = 96$ g of oxygen.

or, $3 \times 6{\cdot}023 \times 10^{23}$ oxygen molecules weigh 96 g.

$$\therefore \quad \text{1 oxygen molecule weighs } \frac{96}{3 \times 6{\cdot}023 \times 10^{23}} = 5{\cdot}32 \times 10^{-23}\text{ g.}$$

$$\text{2 oxygen atoms weigh } \quad 5{\cdot}32 \times 10^{-23}\text{ g}$$

$$\therefore \quad \text{1 oxygen atom weighs } \quad \frac{5{\cdot}32}{2} \times 10^{-23}\text{ g} = 2{\cdot}66 \times 10^{-23}\text{ g.}$$

(*b*) Mol. wt. of $CO_2 = 44$. 1 gram mole $CO_2 = 44$ g

At N.T.P. vol. of 44 g of CO_2 = 22·4 litre

Again, Mol. wt. of $NH_3 = 17$, 1 gram mole of $NH_3 = 17$ g

or, at N.T.P. vol. of 17 g of NH_3 = 22·4 litre

Thus, it is found that under the same conditions of temperature and pressure i.e., at N.T.P. equal volumes i.e., 22·4 litre of CO_2 and NH_3 weigh 44 g and 17 g respectively.

i.e., CO_2 is $\frac{44}{17} = 2{\cdot}59$ times heavier than NH_3.

2. *The volume of 0·02016 g of a gas at N.T.P. is 224 ml. Find the weight of 1 molecule of the gas.*

Ans : The wt. of 224 ml gas at N.T.P. is 0·02016 g

$$\therefore \text{ The wt. of 22400 ml gas at N.T.P. is } \frac{0{\cdot}02016 \times 22400}{224} = 2{\cdot}016\text{ g}$$

or, the gram molecular wt. of the gas = 2·016 g

Hence the number of molecules present in this weight of the gas is $6{\cdot}023 \times 10^{23}$

$$\text{or, the wt. of 1 molecule of the gas } = \frac{2{\cdot}016}{6{\cdot}023 \times 10^{23}} = 3{\cdot}347 \times 10^{-24}\text{ g}$$

3. *There are 3 gas jars kept at the same temperature and pressure. The first jar contains 2·0 litre of CO_2, the second 5·0 litre of hydrogen while the 3rd gas jar contains 7·0 litre oxygen. The number of CO_2 molecule in the first gas jar was found to be $2{\cdot}4 \times 10^{22}$. Find the number of molecules of hydrogen and oxygen in the second and the third gas jars.*

Ans : From Avogadro's law, we know that under the same conditions of temperature and pressure equal volume of all gases contain equal number of molecules. Hence 2 litre of CO_2 or 2 litre of hydrogen or 2 litre of oxygen will contain the same number of molecules.

$\therefore$ Number of molecules of hydrogen in 2 litre = $2{\cdot}4 \times 10^{22}$

or " " " " " 5 " = $\dfrac{2{\cdot}4 \times 10^{22} \times 5}{2} = 6 \times 10^{22}$

Again the number of oxygen molecule in 2 litre = $2{\cdot}4 \times 10^{22}$

$\therefore$ " " " " " 7 " = $\dfrac{2{\cdot}4 \times 10^{22} \times 7}{2} = 8{\cdot}4 \times 10^{22}$

4. (i) *If the density of water is 1 g/ml find the total number of water molecules present in 1 litre of water.*

(ii) *What is the weight of 1 molecule of water ?*

(iii) *Calculate the number of hydrogen atoms in 1·7 g of NH_3.*

(iv) *Find the number of nitrogen and hydrogen atoms in 0·112 litre of NH_3 at N.T.P.*

Ans : (i) Since the density is 1 g/ml, the weight of 1 lit or 1000 ml of water $= 1000\times1 = 1000$ g.
Again 1 g mole of water = 18 g.
or, 18 g of water contain $6{\cdot}023\times10^{23}$ molecules
1000 g " " " $\frac{6{\cdot}023\times10^{23}\times1000}{18} = 334{\cdot}61\times10^{23}$ molecules

(ii) The wt. of $6{\cdot}023\times10^{23}$ molecules of water = 18 g
$\therefore$ wt. of 1 molecule $= \frac{18}{6{\cdot}023\times10^{23}}$ gm $= 2{\cdot}99\times10^{-23}$ g

(iii) 1 g mole NH_3 = 17 g
17 g NH_3 contain $6{\cdot}023\times10^{23}$ molecules of NH_3
$\therefore$ 1·7 " " " $\frac{6{\cdot}023\times10^{23}\times1{\cdot}7}{17} = 6{\cdot}023\times10^{22}$ molecules

1 NH_3 molecule contains 3 atoms of hydrogen.
$\therefore$ The number of hydrogen atoms in 1·7 g of $NH_3 = 6{\cdot}023\times10^{22}\times3$
$= 18{\cdot}069\times10^{22}$

(iv) At N.T.P. 22·4 litre of NH_3 contain $6{\cdot}023\times10^{23}$ molecules
$\therefore$ " " 0·112 litre of NH_3 contains $\frac{6{\cdot}023\times10^{23}\times0{\cdot}112}{22{\cdot}4}$ molecules
$= 3{\cdot}0115\times10^{21}$ molecules.

NH_3 molecule contains 1 atom of nitrogen and 3 atoms of hydrogen.
$\therefore$ Number of nitrogen atoms $= 3{\cdot}0115\times10^{21}$
$\therefore$ " " hydrogen " $= 3\times3{\cdot}0115\times10^{21} = 9{\cdot}0345\times10^{21}$

5. *On the basis of Avogadro's law, answer the following questions :*
(a) *Find the volume of 8 g of SO_2 at S.T.P.*
(b) *What is the weight of 2·8 litre of H_2S at S.T.P ?*
(c) *The volume of 0·7 g of a volatile compound at S.T.P. is 140 ml. Find its molecular weight.*
(d) *Find the weight of H_2SO_4 present in 2 moles of it ?*
(e) *Find the number of moles of sodium atom present in 0·23 g of sodium.*
(f) *Find the number of oxygen atom in 0·9 g of water.* [*H.S. 1978*]

Ans : (a) Mol. wt. of SO_2 = 64 g
$\therefore$ 1 gram mole of SO_2 = 64 g
$\therefore$ At S.T.P. the vol. of 64 g of SO_2 = 22·4 litre
$\therefore$ " " " " " 8 " " " $= \frac{22{\cdot}4\times8}{64} = 2{\cdot}8$ lits.

(b) Mol. wt. of H_2S = 34 g
$\therefore$ At S.T.P. the wt. of 22·4 litre of H_2S is 34 g
$\therefore$ " " " " " 2·8 " " " $= \frac{34\times2{\cdot}8}{22{\cdot}4} = 4{\cdot}25$ g

(c) At S.T.P. the wt. of 140 ml of the compound is 0·7 g
" " " " 22400 " " " $\frac{0{\cdot}7\times22400}{140} = 112$ g
or, the molecular weight of the compound is 112.

(d) Molecular weight of H_2SO_4 = 98
or, 98 g of H_2SO_4 = 1 gram mole or 1 mole of H_2SO_4
or, 2 moles of $H_2SO_4 = 2\times98 = 196$ g of H_2SO_4

(e) Atomic weight of Sodium = 23
1 mole sodium = 23 g of sodium
or 23 g sodium = 1 mole
or 0·23 g sodium $= \frac{0{\cdot}23}{23} = 0{\cdot}01$ mole sodium.

(f) The molecular weight of water = 18
or, 1 g mole of H_2O = 18 g
18 g of H_2O contain $6{\cdot}023\times10^{23}$ molecules of H_2O
0·9 g H_2O contains $\frac{6{\cdot}023\times10^{23}\times0{\cdot}9}{18} = 3{\cdot}0115\times10^{22}$ molecules.
Since 1 molecule of H_2O contains 1 atom of oxygen,
the number of oxygen atoms = $3{\cdot}0115\times10^{22}$

6. *Determine the number of molecules present in hydrogen gas which is liberated by the action of excess of dilute H_2SO_4 on 1 g of magnesium.* [*W.B.H.S. 1976*]

Ans : Equation of the reaction is :

$$\underset{24\ g}{Mg} + H_2SO_4 = MgSO_4 + \underset{2\ g}{H_2}$$

24 g of Mg liberate 2 g of hydrogen
or, 1 g of Mg liberates $\frac{1}{12}$ g of hydrogen
Again 1 gram mole or 2 g of hydrogen contain $6{\cdot}023\times10^{23}$ molecules of hydrogen.
$\therefore\ \frac{1}{12}$ g of hydrogen will contain $\frac{6{\cdot}023\times10^{23}}{2\times12}$ molecules = $0{\cdot}25\times10^{23}$ molecules.

7. *Calculate the number of moles and molecules left behind when 10^{20} molecules are removed from 0·17 g of NH_3.*

Ans : Gram-mole of NH_3 = 17 g
$6{\cdot}023\times10^{23}$ molecules of NH_3 are present in 17 g of NH_3
$\therefore\ 10^{20}$ " " " " " " $\frac{17\times10^{20}}{6{\cdot}023\times10^{23}} = 0{\cdot}0028$ g of NH_3
The remaining weight of $NH_3 = (0{\cdot}17-0{\cdot}0028) = 0{\cdot}1672$ g
0·1672 g $NH_3 = \frac{0{\cdot}1672}{17} = 0{\cdot}00983$ mole
Again, 1 mole NH_3 contains $6{\cdot}023\times10^{23}$ molecules
0·00983 " " $6{\cdot}023\times10^{23}\times0{\cdot}00983 = 5{\cdot}920\times10^{21}$ molecules

8. *Determine the number of water molecules present in 1 drop of water having a diameter 2 mm. Given, density of water is 0·9 g/c.c.* [*I.I.T. '83*]

Ans : The radius of the drop of water = 1 mm = 0·1 cm
$\therefore$ The vol. of the drop = $\frac{4}{3}\pi r^3 = \frac{4}{3}\times\frac{22}{7}\times(0{\cdot}1)^3$ c.c.

The weight of the drop = volume × density = $\frac{4}{3}\times\frac{22}{7}\times(0{\cdot}1)^3\times0{\cdot}9$ g
1 gram mole of water = 18 g
18 g of water contain $6{\cdot}023\times10^{23}$ molecules of water
$\frac{4}{3}\times\frac{22}{7}\times(0{\cdot}1)^3\times0{\cdot}9$ " $\frac{6{\cdot}023\times10^{23}\times4\times22\times(0{\cdot}1)^3\times0{\cdot}9}{3\times7\times18}$ molecules
$= 1{\cdot}26\times10^{20}$ molecules.

9. *Determine the number of oxygen molecules present in 1 litre at 0°C and $7{\cdot}6\times10^{-10}$ mm pressure.*

Ans : Let the volume of oxygen at N.T.P. be *V* litre
$\frac{760\times V}{273} = \frac{1\times7{\cdot}6\times10^{-10}}{273}$ or, $V = 10^{-12}$ litre

22·4 litre of oxygen at N.T.P. contain $6{\cdot}023\times10^{23}$ molecules
$\therefore\ 10^{-12}$ litre " " " " $\frac{6{\cdot}023\times10^{23}\times10^{-12}}{22{\cdot}4}$ molecules
$= 2{\cdot}69\times10^{10}$ molecules.

10. *Find the volumes of 0·25 g atom of chlorine gas at N.T.P.*

Ans : The volume of 1 gram mole chlorine gas at N.T.P. is 22·4 litre

Hence volume of 1 gram atom chlorine gas at N.T.P. $\frac{22{\cdot}4}{2}=11{\cdot}2$ litre

[chlorine is diatomic]

∴ The volume of 0·25 g atom of chlorine gas at N.T.P. = $0{\cdot}25\times11{\cdot}2$ litre = 2·8 litre.

11. *Calculate the weight of HNO_3 in g which contain the same number of molecules as in 24·5 g of H_2SO_4*

Ans : 98 g of H_2SO_4 contain $6{\cdot}023\times10^{23}$ molecules

24·5 g of H_2SO_4 contain $\frac{6{\cdot}023\times10^{23}\times24{\cdot}5}{98}$ molecules = $1{\cdot}50575\times10^{23}$ molecules

Gram molecular weight of HNO_3 = 63 g

∴ $6{\cdot}023\times10^{23}$ molecules of HNO_3 are present in 63 g of HNO_3

$1{\cdot}50575\times10^{23}$ " " " " " " $\frac{63\times1{\cdot}50575\times10^{23}}{6{\cdot}023\times10^{23}}$ g

= 15·75 g of HNO_3

12. *Given that the weight of 350 ml of a diatomic gas at 0°C and 2 atmosphere pressure is 1 g. Calculate the weight of 1 atom of the gas in grams.* [*I.I.T. 1970*]

Ans : Let the vol. of the gas at N.T.P. be V ml

$\frac{1\times V}{273}=\frac{2\times350}{273}$ or, $V=700$ ml.

The wt. of 700 ml of the gas at N.T.P. is 1 g

∴ " " 22400 " " " " " $\frac{1\times22400}{700}=32$ g

∴ The mol. wt. of the gas = 32.

∴ The wt. of 1 molecule of the gas = $\frac{32}{6{\cdot}023\times10^{23}}$ g

Since the gas is diatomic, one molecule of the gas will contain 2 atoms.

∴ The wt. of 2 atoms of the gas = $\frac{32}{6{\cdot}023\times10^{23}}$ g

∴ The wt. of 1 atom of the gas = $\frac{32}{2\times6{\cdot}023\times10^{23}}$ g = $2{\cdot}656\times10^{-23}$ g.

13. (a) *Calculate the number of electrons in 18 ml of water.*

(b) *Find the total number of neutrons and the total mass of neutrons in 7 mg of C^{14} (assume that the mass of a neutrons = mass of a hydrogen atom)* [*I.I.T. 1980*]

Ans : (a) One molecule of water contains 2 atoms of hydrogen and one atom of oxygen. Again 2 atoms of hydrogen contain 2 electrons and 1 atom of oxygen contains 8 electrons (atomic number of oxygen = 8). Hence the total number of electrons present in one molecule of water = 10.

Since the density of water is 1 g/ml, 18 ml will contain 18 g of water.

Now 18 g of water = 1 gram mole of water.

18 g of water contain $6{\cdot}023\times10^{23}$ molecules of water

Since each molecule of water contains 10 electrons,

the total number of electrons present = $6{\cdot}023\times10^{23}\times10=6{\cdot}023\times10^{24}$

(b) The atomic number of $C^{14}=6$

Hence the number of neutrons = 14 − 6 = 8

Again the number of moles of C^{14} atom in 7 mg of C^{14}

$\frac{\text{Weight}}{\text{Atomic mass}}=\frac{7\times0{\cdot}001}{14}=0{\cdot}5\times0{\cdot}001=5\times10^{-4}$

One mole of C^{14} contains $6{\cdot}023\times10^{23}$ atoms.

Hence the total number of neutrons $= 8 \times 5 \times 10^{-4} \times 6{\cdot}023 \times 10^{23}$
$= 24{\cdot}09 \times 10^{20}$

Again the weight of 1 atom of hydrogen $= \dfrac{1{\cdot}008}{6{\cdot}023 \times 10^{23}} = 0{\cdot}16 \times 10^{-23}$ g.

The total mass of neutron $= 24{\cdot}09 \times 10^{20} \times 0{\cdot}16 \times 10^{-23}$ g $= 3{\cdot}85 \times 10^{-3}$ g.

14. *Which one is more heavy—1 gram mole of NO or 0·5 gram mole of NO_2 ? Calculate the number of nitrogen atoms in each ? Calculate the mass of 1 atom of nitrogen.* [*W.B.H.S. 1981*]

Ans : The mol. wt. of NO = 30
The mol. wt. of NO_2 = 46
1 gram mole of NO = 30 g
1 gram mole of NO_2 = 46 g
0·5 gram mole of NO_2 = 46×0·5 = 23 g

Hence 1 gram mole of NO is heavier than 0·5 gram mole of NO_2.

1 gram mole of NO i.e., 30 g of NO contain $6{\cdot}023 \times 10^{23}$ nitrogen atoms
Again 1 gram mole of NO_2 contains $6{\cdot}023 \times 10^{23}$ atoms of nitrogen
0·5 gram mole of NO_2 contains $6{\cdot}023 \times 10^{23} \times 0{\cdot}5 = 3{\cdot}01115 \times 10^{23}$ atoms of nitrogen

The mass of 1 atom of nitrogen $= \dfrac{\text{At. wt. of Nitrogen}}{\text{Avogadro's number}} = \dfrac{14}{6{\cdot}023 \times 10^{23}}$
$= 2{\cdot}32 \times 10^{-23}$ g.

15. (a) *Calculate the number of moles in 1 litre water.* [*W.B.J.E.E. 1983*]
(b) *Find the number of moles and molecules in 56 g of nitrogen.* [*W.B.H.S. 1978*]
(c) *What is the number of water molecules in 1·8 c.c. water ?* [*W.B.H.S. 1984*]

Ans : (a) Since the density of water is 1 g/ml, the weight of 1000 ml or 1 litre of water is 1000 g. 1 gram mole of water = 18 g.

∴ the number of moles of water is 1000 g water $= \dfrac{1000}{18} = 55{\cdot}5$ moles

(b) 1 gram mole of nitrogen = 28 g

or, 56 g of nitrogen $= \dfrac{56}{28} = 2$ moles of nitrogen.

1 mole nitrogen gas contains $6{\cdot}023 \times 10^{23}$ molecules of nitrogen
2 moles " " " $2 \times 6{\cdot}023 \times 10^{23}$
$= 12{\cdot}046 \times 10^{23}$ molecules

(c) The weight of 1·8 ml water = 1·8 g

The number of moles $= \dfrac{\text{weight}}{\text{mol. wt.}} = \dfrac{1{\cdot}8}{18} = 0{\cdot}1$ mole.

1 mole of water contains $6{\cdot}023 \times 10^{23}$ molecules of water
0·1 mole of water contains $0{\cdot}1 \times 6{\cdot}023 \times 10^{23}$ molecules of water
$= 6{\cdot}023 \times 10^{22}$ molecules.

16. *Equal masses of two gases A and B are kept in two separate vessels at the same temperature and pressure. If the ratio of the molecular weights of A and B be 2 : 3 ; find the ratio of the volumes of the two vessels.* [*W.B.H.S. 1982*]

Ans : Let the mol. wt. of *A* and *B* be 2*x* and 3*x* respectively.
∴ the vol of 2*x* g of *A* is 22·4 litre at N.T.P.
and the vol of 3*x* g of *B* is 22·4 litre at N.T.P.
If the vol of 3*x* g of *B* at N.T.P. be 22·4 litre
If the vol of 2*x* g of *B* at N.T.P. be $\dfrac{22{\cdot}4 \times 2x}{3x}$ litre $= \dfrac{22{\cdot}4 \times 2}{3}$ litre

or, $\dfrac{\text{Volume of } A}{\text{Volume of } B}$ of equal weight $= \dfrac{22{\cdot}4}{\dfrac{22{\cdot}4\times 2}{3}} = \dfrac{3}{2}$

Hence, the vol ratio is 3 : 2, i.e., the reverse.

17. *A mixture of hydrogen and oxygen contains 20% by weight of hydrogen. What is the total number of molecules present per gram of the mixture ?* [*W.B.H.S. 1983*]

Ans : Percentage of hydrogen by wt. = 20

" " oxygen " " = 80

Weight of hydrogen in 1 g of the mixture $= \dfrac{20}{100} = \dfrac{1}{5}$ g.

Weight of oxygen in 1 g of the mixture $= \dfrac{80}{100} = \dfrac{4}{5}$ g.

Now 2 g of hydrogen contain $6{\cdot}023\times10^{23}$ molecules of hydrogen

$\dfrac{1}{5}$ g " " contains $\dfrac{6{\cdot}023\times10^{23}}{2\times5} = 6{\cdot}023\times10^{22}$ molecules.

Again 32 g of oxygen contain $6{\cdot}023\times10^{23}$ molecules of oxygen

$\dfrac{4}{5}$ g " " contains $\dfrac{6{\cdot}023\times10^{23}\times4}{5\times32} = 1{\cdot}50575\times10^{22}$ molecules.

Hence, the total number of molecules in the mixture per gram.

$= 6{\cdot}023\times10^{22} + 1{\cdot}50575\times10^{22} = 7{\cdot}52875\times10^{22}$

18. (a) *Find the volume of 1 molecule of water if the density of water be 1 g/c.c.*

(b) *Calculate the diameter of an oxygen atom. Given that the volume of oxygen atom is half that of a molecule of water.* [*I.I.T. 1969*]

Ans : (a) The molecular weight of water = 18

∴ 18 g water = 1 gram mole water

The volume of 18 g water $= \dfrac{\text{Mass}}{\text{density}} = \dfrac{18}{1} = 18$ c.c.

The number of molecules of water present in 18 g of water = Avogadro number $= 6{\cdot}023\times10^{23}$.

The vol. of $6{\cdot}023\times10^{23}$ molecules of water = 18 c.c.

" " " 1 molecule " " $\dfrac{18}{6{\cdot}023\times10^{23}} = 2{\cdot}988\times10^{-23}$ c.c.

(b) Let the radius of an oxygen atom be r cm.

The volume $= \dfrac{4}{3}\pi r^3$ (assuming oxygen atom to be spherical)

According to the problem :—

$$\frac{4}{3}\pi r^3 = \frac{1}{2}\times2{\cdot}988\times10^{-23}$$

Solving, $r = 1{\cdot}526\times10^{-8}$ cm.

The diameter of oxygen atom $= 2r = 2\times1{\cdot}526\times10^{-8}$ cm

$= 3{\cdot}052\times10^{-8}$ cm $= 3{\cdot}052$ Å

19. *1 litre of a gaseous element reacts with 2 litre of another gaseous element to form 1 litre of a gaseous compound. (all volumes being measured at the same temperature and pressure). Both the elements are known to be diatomic. Taking the symbols for the two elements as X and Y respectively, find the molecular formula of the compound.* [*W.B.H.S. 1982*]

Ans : Under the same conditions of temperature and pressure, 1 litre of X combines with 2 litre of Y to form 1 litre of the compound of X and Y.

Let n be the number of molecules present per litre of the gas. Hence from Avogadro's hypothesis :

n molecules of X combine with $2n$ molecules of Y to form n molecules of the gaseous compound.

1 molecule of X combines with 2 molecules of Y to form 1 molecule of the gaseous compound.

Since both X and Y are diatomic.

2 atoms of X combine with 4 atoms of Y to form 1 molecule of the compound.

or, 1 molecule of the compound contains 2 atoms of X and 4 atoms of Y.

$\therefore$ The Molecular formula of the compound is X_2Y_4.

20. *The vapour density of a gas is 40. Calculate the volume of 20 g of this gas at 27 °C and 950 mm of pressure.*

Ans : Mol. wt of the gas = 2×40 = 80
1 gram mole of the gas = 80 g.
The vol. of 80 g of gas at N.T.P. = 22·4 litre

$$\text{" " " 20 " " " " "} \quad \frac{22{\cdot}4\times20}{80} = 5{\cdot}6 \text{ litre}$$

Let the volume of 5·6 litre of the gas be V litre at 27°C and 950 mm pressure be V litre.

$$\text{then } \frac{V\times950}{300} = \frac{5{\cdot}6\times760}{273} \quad \text{or, } V = \frac{5{\cdot}6\times760\times300}{950\times273} \text{ litre or, } V = 4{\cdot}9 \text{ litre.}$$

21. *The weight of 1 litre of a gas at 27 °C and 600 mm pressure is 0·8 g. What is its vapour density and molecular weight ?*

Ans : Let the volume of the gas at N.T.P. be V ml

$$\therefore \frac{V\times760}{273} = \frac{1000\times600}{300}$$

or, $V = 718{\cdot}4$ ml

Thus at N.T.P. the weight of 718·4 ml gas is 0·8 g

$$\text{" " " " " 22400 " " "} \quad \frac{0{\cdot}8\times22400}{718{\cdot}4} \text{ g} = 24{\cdot}94 \text{ g}$$

$\therefore$ the gram molecular weight of the gas = 24·94 g.
So, the molecular weight of the gas = 24·94

$$\text{Hence, the vapour density} = \frac{\text{Mol. wt}}{2} = \frac{24{\cdot}94}{2} = 12{\cdot}47.$$

22. *24 g of a solid element require 44·8 litre of oxygen at N.T.P. for its complete conversion into a gaseous oxide. The gaseous oxide occupies a volume of 44·8 litre at N.T.P. What is the weight of the gaseous oxide produced and what is its vapour density ?* [*W.B.H.S. 1984*]

Ans : 22·4 litre of oxygen at N.T.P. correspond to 1 gram mole of oxygen.
$\therefore$ 44·8 litre of oxygen at N.T.P. correspond to 2 gram moles of oxygen or 64 g of oxygen.
Hence, the weight of the gaseous oxide = 24+64=88 g
According to the problem, 88 g of the gaseous oxide occupies a volume of 44·8 litre.
Therefore, the weight 88 g = 2 gram moles of the oxide.

$$\text{Hence, the mol. wt of the oxide} = \frac{88}{2} = 44 \text{ and its vapour density} = 22.$$

23. *When 0·1022 g of a substance is vapourised it occupies a volume of 55·5 c.c. at 27 °C and 750 mm pressure. Calculate its molecular weight.*

Ans : Let V be the volume of the gas at N.T.P.

$$\therefore \frac{V\times760}{273} = \frac{55{\cdot}5\times750}{300} \quad \text{or, } V = 49{\cdot}84 \text{ c.c.}$$

The weight of 49·84 c.c. of the vapour at N.T.P. = 0·1022 g

" " "22400 " " " " " " $\frac{0.1022\times22400}{49.84}=45.93$ g

Hence the gm molecular weight of the gas = 45·93 g.
or, the molecular weight = 45·93

24. *What is the volume of 20 g of a gas at 27°C and 700 mm pressure if its vapour density is 15 ?*

Ans : The molecular wt. of the gas = 2×15 = 30
or, 1 gram mole of the gas = 30 g
So 30 g of the gas at N.T.P. occupy 22·4 litre
20 " " " " " " " " $\frac{22.4\times20}{30}=14.93$ litre.

Let the volume of 14·93 litre gas be *V* litre at 27°C and 700 mm pressure

$$\frac{V\times700}{300}=\frac{14.93\times760}{273}\quad\text{or, } V=17.8\text{ litre.}$$

The volume of 20 g of the gas is 17·8 litre at 27°C and 700 mm pressure.

25. *If the volume of a sample of gas be 0·418 litre at 27°C and 740 mm pressure :*
(i) *Find the volume of the gas at N.T.P.*
(ii) *If the weight of the volume be 3 g what is its molecular weight ?*
(iii) *If the weight of the same volume (0·418 litre) of the gas be increased to 7·5 g and the temperature be decreased to 280 K, what will be the pressure of the gas ?*
[*I.I.T. 1973*]

Ans : (i) Let at N.T.P. the volume of the gas be *V* litre

$$\therefore\ \frac{760\times V}{273}=\frac{740\times0.418}{300}\quad\text{or, } V=0.3704\text{ litre}$$

(ii) At N.T.P. the weight of 0·3704 litre of the gas = 3 g
" " " " " 22·4 " " " " $\frac{3\times22.4}{0.3704}=181.42$ g.

Hence the molecular weight of the gas = 181·42

(iii) For *n* gram mole of an ideal gas

$PV=nRT$ $\qquad$ n = number of gm mole = $\frac{7.5}{181.42}=0.0413$

$$P=\frac{n}{V}RT$$

$$\text{or, } P=\frac{0.0413\times0.082\times280}{0.418}=2.27\text{ Atmosphere}=2.27\times760\text{ mm}=1725.2\text{ mm.}$$

26. *3·7 g of a gas at 25°C occupy the same volume as 0·184 g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas ?*
[*I.I.T. 1979*] [*MLNR '91*]

Ans : For *n* moles of an ideal gas

$PV=nRT$ $\qquad$ W = Weight in g of the gas.
Where $n=\frac{W}{M}$ $\qquad$ M = Molecular wt of the gas.
Given Molecular weight of hydrogen = 2
or $PV=\frac{W}{M}RT$ $\qquad$ The pressure and volume of the gas and hydrogen are same.
R = Universal gas constant.

Now if M_1 and M_2 be the Molecular weights of the gas and hydrogen respectively having weights W_1 and W_2 g ; the temperature being T_1K and T_2K.

$$\frac{W_1}{M_1}RT_1=\frac{W_2}{M_2}RT_2\quad\text{or, }\frac{W_1}{M_1}T_1=\frac{W_2}{M_2}T_2$$

$$\frac{3\cdot7}{M_1}\times298 = \frac{0\cdot184}{2}\times290$$

$$\text{or, } M_1 = \frac{3\cdot7\times298\times2}{0\cdot184\times290} = 41\cdot3268$$

Hence the molecular weight of the gas = 41·3268.

27.(a) *1 volume of hydrogen combines with sulphur to form 1 volume of a gas A whose vapour density is 17. Find the molecular formula of A.*

(b) *The weight of 254·5 ml of a gas at 0°C and 2 atmosphere pressure is 1 g. Calculate the weight of 1 molecule of the gas.*

Ans : (a) 1 volume of the gas *A* contains 1 volume of hydrogen.

Let *n* be the number of molecules present in 1 vol. of the gas.

From Avogadro's law :—

n number of *A* molecules contain *n* molecules of hydrogen

or, 1 molecule of *A* contains 1 molecule of hydrogen

or, 1 " " " " 2 atoms " "

[Since hydrogen molecule is diatomic]

Hence the emperical formula of *A* is H_2S_x where x = Number of sulphur atoms

Since the vapour density of *A* = 17, its mol. wt. = 17×2 = 34

the mol. wt. of $H_2S_x = 2+32.x$

$\therefore\ 2 + 32x = 34$ or, $32x = 32$ or, $x = 1$

Hence the molecular formula of *A* is H_2S.

(b) Let at N.T.P. the vol. of the gas be *V* ml.

$$\therefore\ \frac{V\times1}{273} = \frac{254\cdot5\times2}{273} \qquad \text{or, } V = 509\text{ ml.}$$

Wt. of 509 ml of gas at N.T.P. = 1 g

$$\text{" " } 22400 \text{ " " " " } = \frac{22400}{509} = 44\text{ g}$$

∴ The molecular wt. of the gas = 44

Now 44 g of the gas contain $6\cdot023\times10^{23}$ molecules

$$\therefore\ \text{The wt. of 1 molecule of the gas} = \frac{44}{6\cdot023\times10^{23}} = 7\cdot3\times10^{-23}\text{ g.}$$

28. *An element A forms several compounds. Their vapour densities are 8·5, 15, 22 and 23 respectively. The percentage of A in those compounds are 82·3, 46·57, 63·6 and 60·87 respectively. Calculate the atomic weight of A.*

Ans : The following results are obtained in finding the molecular weight and weight of *A* in 1 mole of each compound.

Compounds of *A*	Vapour density	Molecular weight	Percentage by wt. of *A* in the compound	Wt. of *A* in 1 mole
Compound I	8·5	17	82·3	$\frac{82\cdot3\times17}{100} = 14$
Compound II	15	30	46·57	$\frac{46\cdot57\times30}{100} = 14$
Compound III	22	44	63·6	$\frac{63\cdot6\times44}{100} = 28$
Compound IV	23	46	60·87	$\frac{60\cdot87\times46}{100} = 28$

Since the minimum weight of *A* in different compounds analysed is 14, the atomic weight of *A* is 14.

29. *The ratio of the molecular weights of two gases A and B is 1 : 2. Find the ratio of the number of their molecules present in (a) the same volume of each gas under the same conditions of temperature and pressure and (b) the same mass of each.*

Ans : Let the molecular weights of A and B be x and $2x$ respectively

$\therefore$ x g of A contain $6{\cdot}023\times10^{23}$ molecules of A

$2x$ " " B " $6{\cdot}023\times10^{23}$ " " B

(a) At N.T.P. the vol. of the gas A is x g of A or 1 gram mole of A is 22·4 litre.

Again at N.T.P. the vol. of the gas B is $2x$ gm of B or 1 gm mole of B is also 22·4 litre.

Now the number of molecules in 22·4 litre is the same i.e., $6{\cdot}023\times10^{23}$ or in other words, equal volumes of A and B will contain equal number of molecules when the pressure and temperature remain constant (Avogadro's hypothesis).

$\therefore$ The ratio of the number of molecules present in same volume of A and $B = 1 : 1$

(b) x g of A contain $6{\cdot}023\times10^{23}$ molecules of A

$2x$ " " B " $6{\cdot}023\times10^{23}$ " " B

or, x g of B contain $\dfrac{6{\cdot}023\times10^{23}}{2}$ molecules of B

In other words the ratio of the number of molecules present is the *same weight* of A and B=

$$\frac{6{\cdot}023\times10^{23}}{\dfrac{6{\cdot}023\times10^{23}}{2}} = \frac{2}{1} \quad \text{or}, 2:1$$

30. *One atom of an element A weighs $6{\cdot}644\times10^{-23}$ g. Calculate the number of gram atoms in 40 kg of it.* *[I.I.T. 1975]*

Ans : The Atomic weight of A = Avogadro number × wt. of 1 atom of A.

$= 6{\cdot}023\times10^{23}\times6{\cdot}644\times10^{-23} = 40$

Hence the number of gram atoms of A in 40 kg $= \dfrac{40\times1000}{40} = 1000$

31. *25 c.c. of a gaseous mixture containing nitrogen and nitric oxide is passed through a hot copper tube. The resulting gas has a volume of 20 c.c. Find the percentage of nitrogen and nitric oxide in the original gas mixture (The volumes have been measured under the same conditions of temperature and pressure).*

[Trip. H.S. 1983]

Ans : When the mixture of the gases is passed over hot copper, nitrogen will remain unchanged but NO will be reduced by copper to nitrogen $2Cu + 2NO = 2CuO + N_2$

Let x c.c. of nitrogen be present in the 25 c.c. mixture. Hence the volume of NO in the mixture is $(25 - x)$ c.c.

From the equation under the same conditions of temperature and pressure :

2 vols of NO give 1 vol of nitrogen.

$\therefore$ $(25 - x)$ cc NO will give $\dfrac{25-x}{2}$ cc of nitrogen

The total volume after the reaction $= \left(x + \dfrac{25-x}{2}\right)$ cc or, $x + \dfrac{25-x}{2} = 20.$

or, $x = 15$ cc

So the mixture contains 15 cc nitrogen and $(25 - 15) = 10$ cc NO

Hence the percentage of nitrogen $= \dfrac{15\times100}{25} = 60$

and the percentage of NO $= \dfrac{10\times100}{25} = 40$

32. *Air contains 21% O_2 and 79% N_2 by volume. Calculate the density of air in g/litre at 27 °C and 760 mm pressure.* [I.I.T. 1962]

Ans : 100 ml of air contain 21 ml O_2 and 79 ml of N_2
Hence 1000 ml air will contain 210 ml O_2 and 790 ml N_2.
The weight of 22400 ml of O_2 at N.T.P. = 32 g

,, ,, ,, 210 ,, ,, ,, ,, ,, ,, $= \frac{32\times210}{22400}$ g = 0·3g

Again the weight of 22400 ml of N_2 at N.T.P. = 28 g

,, ,, 790 ,, ,, ,, ,, $= \frac{28\times790}{22400}$ =0·9875 g

Hence at N.T.P. the weight of 1000 ml or 1 litre of air = (0·3 + 0·9875) = 1·2875 g.
Let V litre be the vol. of air of 27°C and 760 mm pressure

$$\frac{760\times V}{300} = \frac{1\times760}{273} \text{ or, } V = \frac{300}{273} = 1{\cdot}099 \text{ litre}$$

Hence at 27°C and 760 mm pressure 1·099 litre of air weigh 1·2875 g.

1 litre of air weighs $\frac{1{\cdot}2875}{1{\cdot}099} = 1{\cdot}1715$ g

Hence the density of air = 1·1715 g/litre.

33. *When 2·0 g of a gas A was introduced into a vacuum flask at 25°C, the pressure of the gas was found to be 1 atmosphere. Now 3·0 g of another gas B was introduced into the same flask. The total pressure becomes 1·5 atmospheres. Calculate the ratio of the molecular weights of A and B.* [I.I.T. 1977, '83]

Ans : Let the mol. wts. of A and B be x and y respectively.

The number of moles of $A = \frac{2}{x}$ and number of moles of $B = \frac{3}{y}$

When only the gas A is inside the flask, the number of moles $= \frac{2}{x}$ and the pressure = 1 atmosphere, but when both A and B are inside the flask, the total number of moles $= \frac{2}{x} + \frac{3}{y}$ and the total pressure = 1·5 atmosphere.

Now the volume and the temperature of the 2 gases being the same

from, $PV = nRT$ in the first case $1 \times V = \frac{2}{x} RT$ ... ... (i)

in the 2nd case $1{\cdot}5 \times V = \left(\frac{2}{x} + \frac{3}{y}\right) RT$ ... ... (ii)

Dividing (i) by (ii)

$$\frac{1V}{1{\cdot}5V} = \frac{\frac{2}{x}\,RT}{\left(\frac{2}{x}+\frac{3}{y}\right)RT} \quad \text{or,} \quad \frac{1}{1{\cdot}5} = \frac{2xy}{x(2y+3x)} \quad \text{or, } 2y + 3x = 3y$$

or, $3x = y$ or, $x/y = 1/3$

34. *Analysis of a gaseous compound of phosphorous shows that 1 litre of it at N.T.P. never contains less than 1·384 g of the element. Again 1 litre of phosphorous vapour at N.T.P. weighs 5·536 g. What conclusion can be drawn regarding the approximate atomic weight, molecular weight and atomicity of phosphorous from the above results ?* [W.B.J.E.E. 1982]

Ans : 1 litre phosphorous vapour at N.T.P. weighs 5·536 g
∴ 22·4 litres ,, ,, ,, ,, weighs 22·4×5·536 = 124·0064 g
Hence the Molecular weight of Phosphorous = 124·0064

Again at N.T.P. the *minimum* amount of phosphorous present per litre of phosphorous compound is 1·384 g.

Hence at N.T.P. the minimum amount of phophorous present per 22·4 litre of phosphorous compound is $1\cdot384\times22\cdot4 = 31\cdot0016$ g.

Since at least 1 atom of phosphorous *must be* present in 1 molecule of compound, the atomic weight of phosphorous = 31·0016.

Hence the atomicity of phosphorous $= \dfrac{124\cdot0064}{31\cdot0016} = 4$

35. (a) *How many atoms will be present in 0·05 mole of ozone ?* *[W.B.H.S. 1985]*

(b) *Is the number of molecule in one mole of a gas at 100°C and 300 mm pressure equal to, greater than or less than the Avogadro's number ?* *[W.B.H.S. 1983]*

Ans : (a) 1 mole of ozone contains $6\cdot023\times10^{23}$ molecules

$\therefore$ 0·05 ,, ,, ,, ,, $0\cdot05\times6\cdot023\times10^{23}$,,

$= 3\cdot0115\times10^{22}$,,

Now ozone is triatomic molecule, hence the number of atoms present in 0·05 mole. $= 3\times3\cdot0115\times10^{22} = 9\cdot0345\times10^{22}$

(b) 1 mole of any gas (elementary or compound) always contains Avogadro's number or $6\cdot023\times10^{23}$ molecules of the gas. Although the change of pressure or temperature can change the volume of a given mass of gas, its number of molecules remains constant.

- **Calculation according to the Mole concept.**

While working on chemical problems in terms of moles, the following points must be remembered :

(1) The weight of 1 atom of an element $= \dfrac{\text{Gram atomic wt.}}{6\cdot023\times10^{23}}$ g.

(2) The weight of 1 molecule in a given weight of a substance $= \dfrac{\text{Gram Mol. wt.}}{6\cdot023\times10^{23}}$ g

(3) The number of molecules in a given weight of a substance =

$$= \frac{\text{Wt. of the substance in gram}}{\text{Gram Mol. wt.}}\times6\cdot023\times10^{23}$$

(4) The number of atoms in a given weight of an element

$$= \frac{\text{wt. of the element in gram}}{\text{Gram atomic weight}}\times6\cdot023\times10^{23}$$

(5) The number of molecules in *V* litres of gas at N.T.P.

$$= \frac{\text{Volume of the gas in litre}}{22\cdot4\text{ litre}}\times6\cdot023\times10^{23}$$

(6) Number of Gram atom $= \dfrac{\text{Weight of the element in gram}}{\text{Atomic weight}}$

(7) Number of Gram mole or mole $= \dfrac{\text{Weight of the compound in gram}}{\text{Molecular weight}}$

(8) 1 Gram atom or 1 mole atom = Atomic weight expressed in gram.

(9) 1 Gram mole = Molecular weight expressed in gram.

(10) Number of moles of a gas $= \dfrac{\text{Volume of the gas in litre at N.T.P.}}{22\cdot4\text{ litre}}$

36. *The atomic weights of two elements x and y are 12 and 1 respectively. 1 mole x combines with 2 moles y to form 1 mole z. What is the weight of 1 mole z ?*

Ans : Case I. When both the elements *x* and *y* are monoatomic.

1 mole of *x* + 2 moles of *y* = 1 mole of *z*

or, 12 g of *x* + 2 g of *y* = 1 mole of *z*

or, 1 mole of *z* = 12 + 2 = 14 g.

Case II. When *x* is *monoatomic* but *y* is *diatomic*

1 mole of *x* + 2 moles of *y* = 1 mole of *z*

or, 12 g of x + 4 g of y = 1 mole of z
or, 1 mole of z = 12 + 4 = 16 g.

Case III. When both x and y are *diatomic*
1 mole of x + 2 moles of y = 1 mole of z
or, 24 g of x + 4 g of y = 1 mole of z
or, 1 mole of z = 24 + 4 = 28 g.

Case IV When x is *diatomic* but y is *monoatomic*
1 mole of x + 2 moles of y = 1 mole of z
or, 24 g of x + 2 g of y = 1 mole of z
or, 1 mole of z = 24 + 2 = 26 g.

37. ***0·1022 g of a compound is vapourised. The vapour occupies a volume of 55·5 ml at 27 °C and 750 mm pressure. Find the molecular weight of the compound.***

Ans. Let V ml be the volume of the compound at N.T.P.

$$\frac{V\times760}{273}=\frac{55\cdot5\times750}{300}\quad\text{or } V=49\cdot84\text{ ml.}$$

Now at N.T.P. 22400 ml is the volume of 1 mole.

" " 49·84 " " " " $\frac{49\cdot84}{22400}$ mole. = 0·00222 mole.

The weight of 0·00222 mole = 0·1022 g

" " " 1 " $\frac{0\cdot1022}{0\cdot00222}$ = 46 g

or, the gram molecular weight of the vapour = 46 g
∴ the Mol. wt. = 46.

38. ***How much water in gram will be formed when an electric spark is sent to a mixture of 5 g of hydrogen and 50 g of oxygen ? How much oxygen will be left unreacted ?***

Ans :

$$\underset{\text{2 moles}}{2H_2}+\underset{\text{1 mole}}{O_2}=\underset{\text{2 moles}}{2H_2O}.$$

Now 5 g of H_2 = $\frac{5}{2}$ moles

and 50 g of O_2 = $\frac{50}{32}=\frac{25}{16}$ moles

On the basis of the above equation :—
2moles of hydrogen combine with 1 mole of oxygen
1 mole " " combines " $\frac{1}{2}$ " " "
$\frac{5}{2}$mole " " combines " $\frac{1}{2}\times\frac{5}{2}$ " " $=\frac{5}{4}$ moles of oxygen

∴ $\frac{25}{16}-\frac{5}{4}=\frac{5}{16}$ mole of oxygen will remain unreacted.

or, $\frac{5}{16}\times32=10$ g " " " "

Again 2 moles of hydrogen on combustion form 2 moles of H_2O

$\frac{5}{2}$ " " " " " " $\frac{5}{2}$ " " "

or, $\frac{5}{2}$mole of H_2O = $\frac{5}{2}\times18$ = *45 g of H_2O will be formed*

39. ***Calculate the number of moles of $KClO_3$ which will give sufficient oxygen that will completely oxidise 4 moles of hydrogen into water.***

Ans :

$$\underset{\text{2 moles}}{2KClO_3}=2KCl+\underset{\text{3 moles}}{3O_2}$$

$$\underset{\text{2 moles}}{2H_2} + \underset{\text{1 mole}}{O_2} = \underset{\text{2 moles.}}{2H_2O}$$

2 moles of hydrogen are oxidised by 1 mole of oxygen
4 " " " " " " 2 moles of oxygen
Again 3 moles of O_2 are obtained from 2 moles of $KClO_3$
$\therefore$ 2 " " " " " " $\frac{2}{3}\times 2 = \frac{4}{3}$ moles

Hence the required number of moles of $KClO_3 = \frac{4}{3}$

40. *Calculate the amount of copper which on reaction with Conc. H_2SO_4 produces 50 ml of SO_2 at 27 °C and 750 mm pressure.*

Ans : $$\underset{\text{1 mole}}{Cu} + 2H_2SO_4 = CuSO_4 + \underset{\text{1 mole}}{SO_2} + 2H_2O$$

Let the volume of SO_2 at N.T.P be *V* ml

$$\therefore \frac{760\times V}{273} = \frac{50\times 750}{300} \text{ or } V = 44{\cdot}9 \text{ ml.}$$

22400 ml of SO_2 at N.T.P. is produced by 1 mole of Cu
44·9 " " " " " " " " $\frac{44{\cdot}9}{22400} = 0{\cdot}002$ mole of Cu.
Now 0·002 mole of Cu $= 0{\cdot}002 \times 63{\cdot}5$ g $= 0{\cdot}127$ g.

41. *Calculate how much lime will be obtained by heating 500 g of lime stone of 50% purity ?*

Ans : Pure $CaCO_3$ in 500 g of impure lime stone. $= \frac{50\times 500}{100} = 250$ g.
$= \frac{250}{100}$ moles $= 2{\cdot}5$ moles.

$$\underset{\text{1 mole}}{CaCO_3} = \underset{\text{1 mole}}{CaO} + CO_2$$

Since 1 mole of $CaCO_3$ yields 1 mole CaO
hence 2·5 moles of $CaCO_3$ yield 2·5 mole CaO
Now 2·5 moles of CaO $= 2{\cdot}5 \times 56 = 140$ g.
(Mol. wt. of CaO = 56)

42. *Hydrogen is generated by the action of steam on heated magnesium. Calculate the weight of magnesium that will be required to produce just sufficient hydrogen to combine with all the oxygen that can be obtained by the complete decomposition of 24·5 g of $KClO_3$*

Ans :
$$\underset{\text{1 mole}}{Mg} + H_2O = MgO + \underset{\text{1 mole.}}{H_2}$$
$$\underset{\text{2 moles}}{2H_2} + O_2 = \underset{\text{1 mole}}{2H_2O}$$
$$\underset{\text{2 moles}}{2KClO_3} = 2KCl + \underset{\text{3 moles}}{3O_2}$$

From the above equations ; in terms of moles, we have
2 moles of $KClO_3 \equiv$ 3 moles of $O_2 \equiv$ 6 moles of hydrogen $\equiv$ 6 moles of magnesium.
$\therefore$ 1 mole of $KClO_3$ corresponds to 3 moles of Mg.
or, 122·5 g of $KClO_3$ correspond $3\times 24 = 72$ g of Mg.
or, 24·5 " " " " $\frac{72\times 24{\cdot}5}{122{\cdot}5} = 14{\cdot}4$ g.

43. *24·0 g of a mixture of $KClO_3$ and KCl, on being heated produce 7·6 g of oxygen. Calculate the percentage of $KClO_3$ in the mixture.*

Ans : 7·6 g of oxygen = $\frac{7\cdot6}{32} = 0\cdot2375$ mole

The equation of the reaction involved is

$$\underset{2\text{ moles}}{2KClO_3} = \underset{2\text{ moles}}{2KCl} + \underset{3\text{ moles}}{3O_2}$$

3 moles of oxygen are formed from 2 moles of $KClO_3$

∴ 0·2375 ” ” is ” ” $\frac{2\times0\cdot2375}{3} = 0\cdot1583$ mole of $KClO_3$

The molecular weight of $KClO_3 = (39+35\cdot5+3\times16) = 122\cdot5$

∴ 0·1583 mole of $KClO_3 = 0\cdot1583\times122\cdot5 = 19\cdot4$ g.

24 g of the mixture contain 19·4 g of $KClO_3$

100 ” ” ” ” ” $\frac{19\cdot4\times100}{24} = 80\cdot83\%$

44. *The vapour density of a gas is 21·83. What is the volume of 0·393 g of this gas at 27 °C and 750 mm pressure ?*

Ans : The molecular weight of the gas = 2×21·83 = 43·66

$$0\cdot393 \text{ gm of gas} = \frac{0\cdot393}{43\cdot66} = 0\cdot009 \text{ mole.}$$

At 760 mm pressure and 0°C the vol. of 1 mole of any gas = 22·4 litre.

∴ The vol of 0·009 mole of the gas = 22·4 × 0·009 = 0·2016 lit.

Let the volume of 0·2016 lit of the gas at 750 mm pressure and 27°C be *V* litre then

$$\frac{V\times750}{300} = \frac{0\cdot2016\times760}{273}$$

or $V = 0\cdot2245$ litre.

Hence the volume of 0·009 mole of the gas at 27°C and 750 mm pressure is 0·2245 litre.

45. *The hydrogen liberated by treating 0·109 g of a metal with dilute H_2SO_4 at N.T.P. reacts completely with 37·5 ml of O_2 at N.T.P. What is the equivalent weight of the metal ?*

Ans :

$$\underset{(2\text{ moles})}{2H_2} + \underset{(1\text{ mole})}{O_2} = 2H_2O$$

Now 37·5 ml of O_2 at N.T.P. = $\frac{37\cdot5}{22400}$ moles of oxygen

Now from the chemical equation we get,

1 mole of O_2 reacts with 2 moles of hydrogen

or $\frac{37\cdot5}{22400}$ ” ” ” ” ” $\frac{2\times37\cdot5}{22400}$ ” ”

Again 1 g of hydrogen = $\frac{1}{2} = 0\cdot5$ mole

Now, $\frac{2\times37\cdot5}{22400}$ mole of hydrogen is obtained from 0·109 g of the metal

0.5 ” ” ” ” ” ” $\frac{0\cdot109\times22400\times0\cdot5}{2\times37\cdot5}$

$= 16\cdot28$ g

So, by definition the equivalent weight of the metal. = 16·28

46. *The chlorine liberated by the action of 45·3 g of pyrolusite (impure MnO_2) with excess of concentrated HCl, reacts completely with the hydrogen obtained by the action of 10 g of Mg on dilute HCl. Find the percentage of MnO_2 in the Pyrolusite.*

Ans : The equations involved in the above reactions are

$$\underset{(1\,\text{mole})}{MnO_2} + 4HCl = MnCl_2 + 2H_2O + \underset{(1\,\text{mole})}{Cl_2}$$

$$\underset{(1\,\text{mole})}{Mg} + 2HCl = MgCl_2 + \underset{(1\,\text{mole})}{H_2}$$

$$\underset{(1\,\text{mole})}{H_2} + \underset{(1\,\text{mole})}{Cl_2} = \underset{(2\,\text{moles})}{2HCl}$$

The equations show that the Cl_2 obtained from 1 mole of pure MnO_2 combines with 1 mole of hydrogen which is also obtained from 1 mole of Mg.

$10\text{ g of Mg} = \frac{10}{24} = \frac{5}{12}\text{ moles of Mg}$

$\frac{5}{12}\text{ moles of Mg} \equiv \frac{5}{12}\text{ moles of } MnO_2$

Mol. wt. of $MnO_2 = 55+32 = 87$.

Hence $\frac{5}{12}\text{ moles of } MnO_2 = \frac{5}{12} \times 87 = 36{\cdot}25\text{ g of } MnO_2$

Thus 45·3 g of Pyrolusite contain 36·25 g of pure MnO_2

Hence the percentage of pure $MnO_2 = \frac{36{\cdot}25 \times 100}{45{\cdot}3} = 80$

47. *When 0·28 g of Iron powder is added to excess Copper sulphate solution, 0·315 g of metallic Cu is deposited. If the atomic weight of copper is 63 what is the atomic weight of Iron ?*

Ans :

$$\underset{(1\,\text{mole})}{Fe} + CuSO_4 = \underset{(1\,\text{mole})}{Cu} + FeSO_4$$

$0{\cdot}315\text{ g Cu} = \frac{0{\cdot}315}{63}$ mole of Cu.

Let the atomic weight of Fe be x. The number of moles of Fe $= \frac{0{\cdot}28}{x}$

$\frac{0{\cdot}28}{x} = \frac{0{\cdot}315}{63}$ [1 mole of Fe ≡ 1 mole of Cu]

or $x = 56$

∴ The atomic weight of Iron is 56

48. *An organic compound is found to contain 37·4% carbon, 12·6% hydrogen and the rest oxygen. Calculate the number of moles of the organic compound which, on combustion gives CO_2 that converts 5 moles of CaO into $CaCO_3$. (Given that the emperical formula and the molecular formula of the organic compound being the same.)*

Ans : The percentage of oxygen = 100 − (37·4+12·6) = 50

$C:H:O = \frac{37{\cdot}4}{12} : \frac{12{\cdot}6}{1} : \frac{50}{16}$

$= 3{\cdot}116 : 12{\cdot}6 : 3{\cdot}12$

Dividing by the smallest number 3·116 C : H : O = 1 : 4 : 1

So the emperical or the molecular formula of the organic compound is CH_4O or CH_3OH.

The combustion of CH_3OH is given by the equation.

Now

$$\underset{(2\,\text{moles})}{2CH_3OH} + 3O_2 = \underset{(2\,\text{moles})}{2CO_2} + 4H_2O$$

i.e. on complete combustion 2 moles of the organic compound yeild 2 moles of CO_2

$$\text{Again}\quad \underset{(1\,\text{mole})}{CaO} + \underset{(1\,\text{mole})}{CO_2} = CaCO_3$$

Since 1 mole CO_2 is required to convert 1 mole CaO into $CaCO_3$.
Hence 5 moles CO_2 will be required for converting 5 moles CaO into $CaCO_3$
Again 2 moles of CO_2 are obtained from 2 moles of organic compound.
Hence 5 moles of CO_2 are obtained from 5 moles of organic compound.
Hence the required moles of the organic compound = 5

49. *Express in terms of moles the different products obtained when 5·0 g of Blue vitriol are strongly heated. Calculate the number of moles of H_2SO_4 which is obtained from SO_3 in the above reaction.*

Ans : Blue vitriol is $CuSO_4, 5H_2O$
The decomposition reaction of Blue vitriol is

$$CuSO_4, 5H_2O \xrightarrow{250^\circ C} CuSO_4 + 5H_2O\uparrow$$
$$CuSO_4 \xrightarrow{750^\circ C} CuO + SO_3$$

So the total reaction :

$$\underset{(1\,\text{mole})}{CuSO_4, 5H_2O} = \underset{(1\,\text{mole})}{CuO} + \underset{(1\,\text{mole})}{SO_3} + \underset{(5\,\text{moles})}{5H_2O}$$

The molecular weight of $CuSO_4, 5H_2O = 63{\cdot}54 + 32 + 64 + 5\times18 = 249{\cdot}54$

$$\therefore\ 5\text{ g of blue vitriol} = \frac{5}{249{\cdot}54} = 0{\cdot}02\text{ mole}$$

Since the above equation shows that 1 mole of blue vitriol gives 1 mole CuO, 1 mole SO_3 and 5 moles of H_2O
0·02 mole of blue vitriol will give 0·02 mole of SO_3,
0·02 mole of CuO and $5\times0{\cdot}02 = 0{\cdot}1$ mole of H_2O

$$\text{Again}\quad \underset{(1\,\text{mole})}{SO_3} + H_2O = \underset{(1\,\text{mole})}{H_2SO_4}$$

1 mole of SO_3 yields 1 mole of H_2SO_4
∴ 0·02 " " " " 0·02 " " "
The number of moles of $H_2SO_4 = 0{\cdot}02$

50. *What is the weight of (i) $12{\cdot}04\times10^{20}$ atoms of Neon gas. (ii) Br^- ion present in a millimole of $CaBr_2$?*

Ans : (i) 1 mole i.e. $6{\cdot}023\times10^{23}$ atoms of Ne weigh 20·0 g (Atomic weight = Molecular wt. of Ne = 20·0)

$$\therefore\ 12{\cdot}04\times10^{20}\text{ atoms of Ne will weigh} = \frac{20\times12{\cdot}04\times10^{20}}{6{\cdot}023\times10^{23}} = 0{\cdot}03998\text{ g.}$$

(ii) Calcium bromide is an ionic compound. It completely dissociates as

$$\underset{(1\,\text{millimole})}{CaBr_2} = Ca^{++} + \underset{(2\,\text{millimole})}{2Br^-}$$

Since atomic wt. of Br^- is 79·91, 2 millimoles of Br^- ion $= 2\times79{\cdot}91\times10^{-3}$ g $= 0{\cdot}15982$ g.

51. *Find the volume of $6{\cdot}023\times10^{22}$ molecules of Methane at S.T.P.*

[W.B.H.S (Voc) 1979]

Ans : At S.T.P. the volume of $6{\cdot}023\times10^{23}$ molecules of Methane is 22·4 litres.
∴ $6{\cdot}023\times10^{22}$ " " " " " " " "

$$= \frac{22{\cdot}4\times6{\cdot}023\times10^{22}}{6{\cdot}023\times10^{23}}$$
$$= 2{\cdot}24\text{ litres.}$$

52. *If the volume per gram of a gas be 280 millilitres at the standard temperature and pressure, what is its Molecular weight ?* *[W.B.H.S. 1982]*

Ans : At S.T.P. the weight of 280 ml of gas = 1 g.

" " " " 22400 " $\frac{22400}{280} = 80$ g.

According to the definition 1 mole gas = 80 g
Hence the molecular weight of the gas = 80.

53. *What is the volume of 0·25 mole of NH_3 at 0°C and 2 atmosphere pressure ?*

Ans : Volume of 1 mole NH_3 at N.T.P. = 22·4 litres
∴ " " 0·25 " " " " = 22·4×0·25 litres
Applying the Equation

$$\frac{PV}{T} = \frac{P_1 V_1}{T_1}$$

$$\frac{1 \times 22{\cdot}4 \times 0{\cdot}25}{273} = \frac{2 \times V_1}{273} \text{ or } V_1 = 2{\cdot}8 \text{ litres}$$

Hence the required volume = 2·8 litres at 0°C and 2 atmosphere pressure.

54. *Find the number of moles of SO_2 having a volume of 0·224 ml at N.T.P.*

Ans : Volume of 1 mole SO_2 at N.T.P. = 22·4 litres
or 22400 ml of SO_2 at N.T.P. = 1 mole of SO_2

$$0{\cdot}224 \text{ ml} = \frac{0{\cdot}224}{22400} = 10^{-5} \text{ mole of } SO_2$$

55. *Express one atom of an element in terms of mole atom.*

Ans : 1 mole atom = $6{\cdot}023 \times 10^{23}$ atoms.
or, $6{\cdot}023 \times 10^{23}$ atoms of an element = 1 mole atom

$$1 \text{ atom } " \; " \quad " \quad = \frac{1}{6{\cdot}023 \times 10^{23}} \quad "$$

$$= 1{\cdot}66 \times 10^{-24} \text{ mole atom.}$$

• Exercises •

1. State Avogadro's hypothesis. What led to the adoption of this hypothesis ? ***[W.B.H.S. 1991]***

2. State the hypothesis which corelates Gay Lusaac's law of gaseous volume and Dalton's Atomic theory. Discuss the applications of this theory.

3. How can you explain Gay Lusaac's law of gaseous volume with the help of Avogadro's hypothesis ?

4. (a) Show how Avogadro's hypothesis modifies Dalton's atomic theory ?
(b) Can Avogadro's hypothesis be called a law ? Discuss two of the important deductions from this.

5. With the help of Avogadro's hypothesis show that oxygen and chlorine molecules are diatomic.

6. What do you mean by the term vapour density ? Prove that the molecular weight of a gas is twice its vapour density. ***[W.B.H.S. 1980, '83, '91 W.B.J.E.E. '89]***

7. "Equal volumes of all gases at the same temperature and pressure contain the same number of atoms"—
Show that this conclusion of Berzelius was not in agreement with the experimental results. How and why Avogadro corrected the statement ?

8. Write explanatory notes on :
(a) Avogadro's number (b) Gram molecule and Gram atom (c) Molar volume (d) Mole ***[H.S. '93]*** (e) Atomic weight and weight of an atom (f) Molecular theory of matter (g) Elementary and compound molecules.

9. Mention the important deduction made from Avogadro's hypothesis. Discuss two of it.

10. Define atomic weight of an element according to Cannizzero. An element *M* produces several volatile compounds. How could you determine the approximate atomic weight of the element by applying Cannizzero's definition of atomic weight ?

11. Do the density and vapour density (relative density) of a gas depend on the temperature and pressure ? Give the answer in two or three sentences. ***[Joint Ent. 92]***

12. Prove with the help of Avogadro's hypothesis that (i) molecules of hydrogen and oxygen are diatomic (ii) one gram molecule of any gas contains the same number of molecules.

13. Show that at standard temperature and pressure the gram molecular volume of gases usually is 22·4 litre. ***[H.S. '87, '90, 92]***

14. Distinguish between—(a) weight of a molecule of hydrogen and molecular weight of hydrógen, (b) gram molecular weight and molecular weight, (c) molecular weight and molar volume.

15. (a) What is Avogadro's Number ? What is its value ? (b) Establish a relation between normal density and vapour density of a gas.

16. (a) Sulphur dioxide contains its own volume of oxygen. The vapour density of sulphur dioxide is 32. Deduce the molecular formula of sulphur dioxide.

17. (a) How would you prove with the help of Avogadro's hypothesis that if the vapour density of a gas be 16, its molecular weight would be 32 ? (b) What is the difference between density and vapour density of a gas ? ***[Jt. Ent. '88]***

18. What is meant by the unit 'mole' ? What is the advantage of using this unit ? How many moles are present in 1 atom of carbon ? [***Ans.*** 0.166×10^{-23}] ***(W.B.H.S. 1980, '93)***

19. Show the relationship between the following pair of terms.

(a) Molecular weight of chlorine and weight of 1 molecule of chlorine.
(b) 1 kg sodium and 1 kg molecular weight of sodium.
(c) 1 mole N_2 and 1 mole N.

- **Numerical problems :**

1. What is the significance of the number 6.023×10^{23} ?

How can you evaluate the number on the basis of Avogadro's hypothesis ? Given that the absolute weight of hydrogen atom is 1.6734×10^{-24} g. Find the true weight of an atom of oxygen. [***Ans.*** 2.67×10^{-23}g]

2. Express the following in terms of mole :

(a) 219 g of HCl (b) 60 g of HNO_3 (c) 0.9 g of H_2O (d) 0.023 g of sodium. [***Ans.*** 6 moles, 0.9523 mole, 0.05 mole, 0.001 mole]

3. 25 g of Blue vitriol, on strong heating leave a residue of cupric oxide. Show that 0.1 mole of CuO, 0.1 mole of SO_3 and 0.5 mole of H_2O are formed due to heating.

4. The volume of 1 g of a gas at N.T.P. is 500 ml. Determine its vapour density and molecular weight. [***Ans.*** 22.4, 44.8] ***(W.B.H.S. (Comp) 1970)***

5. The weight of 1 litre of a gas at N.T.P. is 3.17 g. What is the molecular weight of the gas ? [***Ans.*** 71] ***(W.B.H.S. 1971)***

6. The weight of 1 atom of an element is found to be 2.008×10^{-23} g. What is the atomic weight of the element ? [***Ans.*** 12.094]

7. The densities of 3 gaseous compounds of an element *X* are 1.25, 1.875 and 2.50 g per litre respectively. Each compound contains six sevenths of its weight of *X*. Calculate the probable atomic weight of *X*. [***Ans.*** 12]

8. The measured vapour, densities of water, nitrous oxide, nitric oxide, acetic acid, carbon dioxide, carbon monoxide and Ozone are 9, 22, 15, 30, 22, 14 and 24 respectively and the percentage by weight of oxygen in these substances are 88.1, 36.4, 53.33, 53.33, 72.75, 57.14 and 100 respectively. What is the probable approximate atomic weight of oxygen ? What further measurements would be necessary to find the accurate atomic weight of oxygen ? [***Ans.*** 16]

9. (a) What will be the volume of 3.20 gram atom of oxygen at N.T.P. [***Ans.*** 2.24 litres] ***(Tripura H.S. 1984)***

(b) Given that the molecular formula of phoshorous is P_4. Calculate the number of (a) gram atoms (b) gram-molecules, (c) atoms, (d) molecule, in 98 g of phosphorous.

[***Ans.*** (a) 3, (b) 0.79, (c) 19.04×10^{23}, (d) 4.764×10^{23}]

10. Calculate (a) the weight (b) the number of molecules (c) the weight of one molecule of 1.4 litres of oxygen at 0°C and 10 mm pressure. [***Ans.*** (a) 0.0263 g, (b) $4{\cdot}9 \times 10^{20}$, (c) 5.31×10^{-23} g]

11. Which one is heavier between 1 mole of sodium and 1 mole of oxygen ? [***Ans.*** Oxygen]

12. (a) What is the weight of oxygen which contains the same number of atoms present in 7.0 g of nitrogen ? [***Ans.*** 8.0 g] ***(Trip. H.S. 1982)***

(b) Calculate the number of water molecules present in 0.5 g of water.

[***Ans.*** 0.167×10^{23}] ***(W.B.H.S. (voc) 1978)***

13. Calculate the weight of copper which contains 10 times of atoms as in 4.0 g of carbon.

[Cu=63] [***Ans.*** 210 g]

14. Which of the following contains the maximum number of atoms.

(i) 0.5 g atom copper (ii) 1.1×10^{22} atoms of copper (iii) 0.435 g of copper [***Ans.*** (i)]

15. When 1 millimole of a chloride of phosporous was completely decomposed by water, 0.430 g of AgCl was precipitated on the addition of excess $AgNO_3$ to this solution. What is the formula for the chloride of phosphorous used in the experiment ? [***Ans.*** PCl_3]

16. What weight corresponds to the following ?
(a) 0.3 mole of hydrogen ion (H^+) (b) 0.3 mole of hydride ion (H^-) (c) 0.6 mole of hydrogen gas
(d) One millimole $CuSO_4 . 5H_2O$. (e) 12.04×10^{20} atoms of calcium.
[*Ans.* (a) 0.3 g, (b) 0.3 g, (c) 1.2 g, (d) 0.2495 g, (e) 0.0799 g]

17. How many moles the following quantities represent
(a) 2 g ice. (b) 3.01×10^{12} alpha particles. (c) 16 g of oxygen gas. (d) 16 g of oxide ion. (e) 48 g of ozone. (f) 20 c.c. benzene of density 0.87 g/c.c.
[*Ans.* (a) 0.11, (b) 5×10^{-12}, (c) 0.5, (d) 1.0, (e) 1.0, (f) 0.223]

18. The weight of 1 litre of a gas at 27°C and 780 mm pressure is 1.215 g. Calculate the vapour density and molecular weight of the gas. [*Ans.* 14.57 and 29.14]

19. An element E forms two hydrides A and B. A and B contains 75% and 80% ot E respectively. The vapour densities of A and B are 8 and 15. One atom of E is present per molecule of A. Calculate : (a) the atomic weight of E and (b) the molecular formula of A and B. [*Ans.* (a) E = 12, (b) EH_4 and E_2H_6]

20. (a) Express the following quantities in terms of mole (i) 292 g HCl, (ii) 50 g HNO_3, (iii) 0.9 g H_2O.
[*Ans.* (i) 8, (ii) 0.79, (iii) 0·05]

(b) Express the following in terms of gram
(i) 2.22 moles of water, (ii) 2 moles of Na, (iii) 0.5 mole of sulphur.
[*Ans.* (i) 39.96 g, (ii) 46 g, (iii) 16 g]

(c) How many moles of nitrogen and oxygen are present in 5 litres at N.T.P.
[*Ans.* O = 0.2232 mole, N = same]

21. The weight of 25 ml of a gas at N.T.P. is 0·7317 g. The density of hydrogen at N.T.P. is 0·8987 g/litre. Determine the vapour density and Molecular weight of the gas.
[*Ans.* 32·56, 65·12] ***(Joint Ent. 1978)***

22. What is the significance of 22·414 litre ? State thc correct results of the following :
(i) The volume in litre of 10 g hydrogen at S.T.P. is (a) 224·14 (b) 2·414 (c) 11·207 (d) 112·071
[*Ans.* d]
(ii) The maximum number of Mg atoms is present in (a) 0·5 g atom of Mg (b) 12 g Mg. (c) 5×10^{23} Mg atoms. [*Ans.* c]
(iii) The minimum number of atom at S.T.P. is present in (a) 1·12 litre SO_2 (b) 1 mole SO_2 (c) 32 g SO_2 (d) 4×10^{23} molecules of SO_2. [*Ans.* a]

23. At S.T.P. 1 litre of oxygen weighs 1·42 g and the density of hydrogen at S.T.P. is ·000089 g/ml. Calculate the atomicity and vapour density of oxygen. [*Ans.* 2 and 16]

24. (a) Calculate the number of moles 2ml NH_3 at N.T.P. [*Ans.* $8{\cdot}9\times10^{-5}$]
(b) How many moles of electron are present in 170 g of NH_3 [*Ans.* 100 mole]
(c) Find the number of molecules of 18 g of water vapour. [*Ans.* $6{\cdot}023\times10^{23}$]

25. (a) Find the weight of 1 atom of oxygen [*Ans.* $2{\cdot}655\times10^{-23}$] ***(Joint Ent. 1983)***
(b) Calculate the weight of 1 atom of nitrogen [*Ans.* $2{\cdot}324\times10^{-23}$] ***(W.B.H.S. 1981)***

26. Find the volume of 2·2 g of carbon dioxide at 27°C and 570 mm pressure.
[*Ans.* 1641 ml] ***(W.B.H.S. 1983)***

27. 44·8 litres of oxygen at N.T.P. were required for the complete conversion of 24·0 g of a solid element into its gaseous oxide. The gaseous oxide occupies a volume of 44·8 litres at N.T.P. Calculate the molecular weight and vapour density of the gaseous oxide. [*Ans.* 88 g, 22] ***(W.B.H.S. 1984)***

28. 3·2 g of sulphur at 45°C and 723 mm pressure when vapourised occupy a volume of 780 ml. What is the molecular formula of the sulphur vapour. [*Ans.* S_8] ***(I.I.T. 1968)***

29. The density of mercury is 13·6 g/c.c. The volume of an atom of mercury is equal to a cube whose length is equal to the diameter of an atom of mercury. What is the diameter of mercury atom.
[*Ans.* $2{\cdot}9\times10^{-8}$] ***(I.I.T. 1983)***

30. A compound containing 2 nitrogen atoms in its molecule has 30·43% nitrogen. Calculate the molecular weight of the compound (N = 14) [*Ans.* 92·01] ***(W.B.H.S. 1985)***

31. Which of the following has the highest mass (a) 20 g of phosphorous (b) 5 moles of water (c) 2 equivalents of sodium carbonate (d) 12×10^{24} atoms of hydrogen. [*Ans.* c] ***(I.I.T. 1978)***

32. Avogadro number of He atoms weighs : (a) 1·00 g (b) 4·00 g (c) 8·00 g (d) $4{\cdot}0\times6{\cdot}023\times10^{23}$ g
[*Ans.* b] ***(I.I.T. 1975)***

33. The volume of 20 g of hydrogen gas at S.T.P. is (a) 224 litres (b) 22·4 litres (c) 2·24 litres (d) 112 litres. [*Ans.* a] ***(I.I.T. 1974)***

34. A compound of carbon, hydrogen and oxygen contains C = 40%, H = 6·67%. When the compound is vapourised, its vapour density is found to be 2·813 times that of oxygen. Find the emperical and the molecular formula of the compound. [*Ans.* CH_2O and $C_3H_6O_3$] ***(W.B.H.S. 1991)***

35. Which of the following has the largest number of molecules and which one has the least ?
(a) 6 g of CO_2 (b) 8 g of oxygen (c) 4 g of nitrogen (d) 2 g of hydrogen ?
[*Ans.* least—4 g of N_2, largest 2 g of H_2] ***(Jt. Ent. '87)***

36. In one drop there are 5×10^{20} molecules of water. If the density of water is 1 g/ml find out the volume of the drop. [***Ans.*** $1{\cdot}5\times10^{-2}$ ml] ***(Jt. Ent. '88)***

37. In a molecule of a compound there are 1 atom of nitrogen and it contains 11·62% of nitrogen. What is the molecular weight of the compound ? [***Ans.*** 120·5]

38. (a) What is the volume of 0·4 gram atom of oxygen of NTP ?
(b) What is mass of $12{\cdot}046\times10^{25}$ number of ammonia molecules ?
[***Ans.*** (a) 4480 ml (b) 3400 g] ***(H.S. '89)***

39. How many atoms of hydrogen and oxygen are present in 0·09 g of water ?
[***Ans.*** $O = 3{\cdot}0115\times10^{21}$, $H = 6{\cdot}023\times10^{21}$] ***(H.S. '93)***

40. At a particular temperature and pressure 10 ml of hydrogen contain 20000 molecules. How many molecules are there in 10 ml of oxygen at that very temperature and pressure ? [***Ans.*** 20000]

41. Calculate the volume occupied by 5·0 g of acetylene gas at 50°C and 740 mm pressure.
[***Ans.*** 5·23 litre] ***(I.I.T. '91)***

42. Calculate how many methane molecules and how many hydrogen and carbon atoms are there in 25 g of methane. [***Ans.*** CH_4—$9{\cdot}411\times10^{23}$, Carbon—$9{\cdot}411\times10^{23}$, H atom—$37{\cdot}644\times10^{23}$] ***(MLNR '90)***

43. Calculate the number of oxalic acid molecules in 100 ml of 0·02N oxalic acid solution.
[***Ans.*** 10^{-3}] ***(Roorke Eng. '91)***

44. Calculate the total number of electrons present in 1·6 g of methane.
[***Ans.*** $6{\cdot}023\times10^{22}$] ***(Roorke Eng. '85)***

45. Equal weights of two substances A & B are taken. The ratio of their atomic weights is 2 : 3.
(a) What is the ratio of molecules in equal weights of these substances ?
(b) If the substances are vaporised, what will be the ratio of their volumes under the same conditions of temperature and pressure ? [***Ans.*** (a) 3 : 2 (b) 3 : 2] ***(Joint Ent. '91)***

46. A 2 litre glass vessel contains N_2 and water vapour in equimolar proportion at 10^{-8} mm Hg pressure and 303 K temperature.
(a) Find out the total number of moles of N_2 and water vapour present.
(b) Find out the total mass of the gas mixture.
(c) What will be the total mass of the gas mixture, if it is cooled to 50°C.
[***Ans.*** (a) $N_2 = 0{\cdot}5\times10^{-7}$, $H_2O = 0{\cdot}5\times10^{-7}$, (b) 23×10^{-7} g, (c) 14×10^{-7} g.] ***(Joint Ent. '91)***

47. What is the mass of 1 millimole of ammonia ? How many number of molecules of ammonia are present in it. [***Ans.*** Mass 0·017 g, $6{\cdot}023\times10^{20}$] ***(Joint Ent. '91)***

48. (a) What is the mole fraction of a solute in a 1·00 molal solution of water. [***Ans.*** 0·0176]
(b) What would be the number of oxygen atoms in a solution containing 3·42 g of glucose in 1·8 g of water. [***Ans.*** $1{\cdot}28\times10^{23}$]

49. What would be the ratio of number of molecules of oxygen and hydrogen in a mixture of these two gases in 2 : 3 proportion by weight ? [***Ans.*** 1 : 24]

50. The volume of one atom of a metal M is $1{\cdot}66\times10^{-23}$ c.c. Find the : atomic weight of M. (Given, density of M = 2·7 g/cc. [***Ans.*** 26·99] ***(Joint Ent. '93)***

51. Calculate the weight in gram of one fluorine atom. [***Ans.*** $3{\cdot}15\times10^{-23}$ g] [*W.B.J.E. '97*]

CHEMICAL EQUATION AND VALENCY

3

Introduction. In order to represent the different elements in short, abbreviations are used in place of their full names for the sake of convenience. These are referred to as symbols of the elements. It was Berzelius (1811) who first introduced the use of modern symbol in chemistry.

3.1. Symbol and formula.

- *A symbol is defined as an abbreviation or short-hand sign for the full name of an element. In other words, the short-hand representation of an atom of an element is known as symbol.*

There are several methods to symbolise an element.

(i) *By using the initial letter of the English name of an element in capital. e.g.,* Hydrogen = H, Oxygen = O, Boron = B, Nitrogen = N etc.

(ii) When the names of two or more elements begin with the same letter they are symbolised *by using the first two letters or by using the initial and another which is prominently heard in pronouncing the word.* The *first letter is always in capital.* e.g., Calcium = Ca, Chromium = Cr, Bromine = Br, Barium = Ba, Argon = Ar, Arsenic = As etc.

(iii) Sometimes the *first letter in capital or the first letter and another letter which is prominently heard in pronouning the Latine name of the element is used as its symbol* e.g.,

Natrium (Sodium) = Na, Kalium (Potassium) = K, Cuprum (Copper) = Cu, Argentum (Silver) = Ag etc.

Significance : A symbol has both qualilative and quantitative significance. Thus,

(i) A symbol is the short representation of an element.

(ii) It denotes an atom of the element. Thus H represents one atom of hydrogen. Similarly 2H and 4H denotes two and four atoms of hydrogen respectively.

(iii) It indicates the number of parts by weight which is equal to the atomic weight of the element. Thus, C represents 1 atom of carbon as well as 12 parts by weight of carbon. Similarly 2N denotes two nitrogen atoms and 28 parts by weight of nitrogen.

(iv) It denotes one gram atom of an element.

- *Formula is the symbolic representation of the molecule of a substance. In other words, the short representation of one molecule of an element or compound is known as formula.*

Significance :

(i) A formula represents the name of an element or a compound.

(ii) It denotes one molecule of a substance (element or compound) and indicates the number of atoms of the constituent elements in the molecule.

(iii) Quantitatively it expresses the molecular weight of a compound.

(iv) It represents the relative weights of the elements present in the molecular weight of the compound. Thus the formula of sulphuric acid is H_2SO_4. This formula denotes that in sulphuric acid 2 parts by weight of hydrogen, 32 parts by weight of sulphur and 64 parts by weight of oxygen are present per 98 parts by weight of H_2SO_4.

(v) The chemical formula also denotes the volume of the gaseous element or compound at N.T.P. e.g., one gram molecule of any gas occupies 22·4 litre at N.T.P. Thus, CO_2 indicates 22·4 litre of CO_2 at N.T.P. $3CO_2$ denotes 3×22·4 litre of CO_2 at N.T.P.

Examples : The formula SO_2 supplies with the following informations :—

(i) The formula SO_2 represents the compound sulphur di-oxide. (ii) It denotes that sulphur di-oxide is made up of one atom of sulphur and two atoms of oxygen. (iii) It represents $32+(2\times16) = 64$ parts (molecular weight) by weight of sulphur di-oxide. (iv) It indicates one gram molecule or one gram mole of sulphur di-oxide. (v) It denotes that 64 parts by weight of sulphur di-oxide contains 32 parts by weight of sulphur and 32 parts by weight of oxygen. (vi) It represents 22·4 litre of sulphur di-oxide at N.T.P.

3.2. Valency.

A chemical compound is formed by the union of two or more elements in a definite proportion by weight. The combining capacity of all the elements are not alike. It is observed that one atom of an element combines with a definite number of atoms of other elements to form a stable compound. Thus, *the number of atoms of an element which can combine with 1 atom of other element is known as its valency or in general combining capacity.*

Analysis of a number of hydrogen compounds shows that excepting hydrazoic acid, no compounds of hydrogen are known where more than one atom of an element combines with one atom of hydrogen. This indicates that the combining capacity of an atom of hydrogen is minimum. Consequently hydrogen atom has been chosen as the standard for measuring the valencies of other elements, i.e., the valency of hydrogen atom is taken as 1.

Hence, *the valency denotes the combining capacity of an atom of an element with the atoms of other elements which is measured by the number of hydrogen atoms, which can combine with or are displaced by one atom of the said element.*

Thus, 1 atom of bromine, 1 atom of oxygen, 1 atom of nitrogen and 1 atom of carbon combines with 1, 2, 3 and 4 atoms of hydrogen to form HBr, H_2O, NH_3 and CH_4 respectively. Hence the valencies of bromine, oxygen, nitrogen and carbon are 1, 2, 3 and 4 respectively.

Compounds of hydrogen	Formula	No. of H-atoms combined with one atom of the element	Valency of the element
Hydrogen bromide	HBr	1	Br = 1
Water	H_2O	2	O = 2
Ammonia	NH_3	3	N = 3
Methane	CH_4	4	C = 4

There are some elements which do not combine directly with H_2, but can displace it from hydrogen compound. The valency of such elements is equal to the number of hydrogen atoms displaced by 1 atom of the element. Thus, 1 atom of magnesium replaces 2 atoms of hydrogen from HCl.

$$Mg + 2HCl = MgCl_2 + 2H\uparrow$$

1 atom of aluminium displaces 3 atoms of hydrogen from HCl.

$$Al + 3HCl \rightarrow AlCl_3 + 3H\uparrow$$

Therefore, the valencies of Mg and Al are 2 and 3 respectively.

There are some elements which are not in a position to combine with hydrogen directly. In these cases the valencies of those elements are determined with reference to chlorine or oxygen.

(i) As 1 atom of hydrogen combines with one atom of chlorine to form HCl, the valency of chlorine is 1. Now 1 atom of zinc combines with 2 atoms of chlorine, hence the valency of Zn is 2. Similarly Al, Sn, P combine with 3, 4 and 5 atoms of chlorine respectively. Hence valencies of Al, Sn, P are 3, 4 and 5 respectively.

(ii) Since 1 atom of oxygen combines with two atoms of hydrogen to form water, oxygen is bivalent. As 1 atom of magnesium combines with 1 atom of oxygen to produce MgO, the valency of Mg is 2. Thus 2 atoms of Al combine with three atoms of oxygen (Al_2O_3). Hence the valency of Al is $\frac{3\times2}{2} = 3$.

Thus, the definition of valency can be modified as follows—*The valency of an element denotes its combining capacity with other elements which is measured by the number of atoms of hydrogen or chlorine or twice the number of atoms of oxygen which can combine with or are displaced by one atom of the said element.*

A stable compound is characterised by the full use of total valencies of all the constituent atoms of the compound. Valency must always be a whole integer —it can never be a fraction.

- **Classifications of elements according to their valencies.**

Elements exhibit valencies from 1 to 8 and accordingly they are classified as *monovalent, divalent, trivalent* and so on.

Classification of some common elements according to their valencies has been shown in the following table.

0 Zerovalent	**1 Monovalent**	**2 Divalent**	**3 Trivalent**	**4 Tetravalent**	**5 Pentavalent**	**6 Hexavalent**	**7 Heptavalent**	**8 Octavalent**
He, Ne Ar, Kr i.e., Inert gases of the atmosphere	H, Cl Br, I F Cu (ous) Hg (ous) Na, K Li, Ag	O, Ca Mg, Zn S, Ba Hg (ic) Fe (ous) Pb (ous) Cu (ic) Sn (ous) Cr (ous) Mn (ous)	N, P, Al Cr (ic) Fe (ic) B, Au As (ous) Bi, Mn	C, Si Sn (ic) Pt, S Pb (ic) Mn	N, P As (ic)	S Se Cr (ate) Mn	Mn Cl	Os Pt

- **Radicals and their valencies.**

A radical or a compound radical may be defined as an atom or a collection of group of atoms which act as a single unit in a chemical reaction but have no separate existance.

There are 3 types of radicals.

(a) **Free radical :** Free radical is a neutral radical which contains an unpaired electron, e.g., Methyl radical ($\cdot CH_3$), Hydrogen radical ($\cdot H$) etc.

(b) **Positively charged radical :** There are some radicals which are positively charged. These radicals may be atom or group of atoms e.g., K^+, Zn^{++}, NH_4^+ etc. During electrolysis, such type of radicals are discharged at the cathode.

(c) **Negatively charged radicals :** There are negatively charged radicals e.g., Cl^-, SO_4^{--}, PO_4^{---}, CO_3^{--} etc. Such type of radicals sometimes display variable valency e.g., $[Fe(CN)_6]$. It may be Ferrocyanide $[Fe(CN)_6]^{----}$ or Ferricyanide $[Fe(CN)_6]^{---}$. In the former case it is tetravalent and in the latter it is trivalent.

The valencies of some familiar radicals are given below :—

Monovalent	Divalent	Trivalent	Tetravalent
Nitrate (NO_3), Cyanide (CN) Nitrite (NO_2), Fluoride (F) Hydroxyl ($\dot{O}H$), Chloride (Cl) Bromide (Br), Iodide (I) Chlorate (ClO_3), Cyanate (CNO) Bicarbonate (HCO_3) Bisulphate (HSO_4) Bisulphite (HSO_3) Aluminate (AlO_2) Metaborate (BO_2) Permanganate (MnO_4)	Sulphide (S) Sulphite (SO_3) Sulphate (SO_4) Carbonate (CO_3) Silicate (SiO_3) Zincate (ZnO_2) Chromate (CrO_4) Dichromate (Cr_2O_7) Thiosulphate (S_2O_3)	Phosphide (P) Phosphate (PO_4) Nitride (N) Ortho borate (BO_3) Ferri cyanide [Fe $(CN)_6$]	Ferro cyanide [Fe $(CN)_6$]

- **Variable valency.**

The valency of an element is not constant. There are some elements which have more than one valency.

According to modern idea valency denotes the number of electrons **lost, gained or shared** by the atom of an element with a view to achieve the configuration of the nearest inert gases. Strictly speaking the number of unpaired electrons in the ground state of an atom indicates its valency but in the excited state if the paired electrons become unpaired and promoted to higher energy level giving rise to different number of unpaired electrons, the element exhibits more than one valency. Thus, valency may not necessarily be constant. For transition elements e.g., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu etc., variable valency is a rule, while constancy in valency is an exception. Normally the suffix *'ous'* is used to denote an element in lower valency and *'ic'* for higher valency. Thus, **monovalent copper—CuCl (Cuprous chloride)** and **bivalent copper—$CuCl_2$ (Cupric chloride).** Similarly Iron is **bivalent (Ferrous)** in FeO, $FeCl_2$, $FeSO_4$, etc., and **trivalent (Ferric)** in Fe_2O_3, $FeCl_3$, $Fe_2(SO_4)_3$ etc. Sulphur is *bivalent* in H_2S, *tetravalent* in SO_2 and *hexavalent* in SO_3.

Variable valencies of some other elements are tabulated below :—

Element	Valency					
	1	2	3	4	5	7
Mercury	Hg_2O	HgO				
Lead		$PbCl_2$ PbO		$PbCl_4$ PbO_2		
Phosphorus			PCl_3 PF_3		PCl_5 PF_5	
Tin		$SnCl_2$		$SnCl_4$		
Chlorine	HCl		$HClO_2$	ClO_2	$KClO_3$	$KClO_4$

- **How to find out the valency of a radical ?**

The valency of a radical can be evaluated by finding the number of hydrogen or chlorine atom with which the radical in question combines e.g., (i) NO_3^- radical unites with 1 atom of H to form HNO_3. Hence the valency of Nitrate radical is 1. (ii)

Again NH_4^+ radical combines with 1 atom of Cl to form NH_4Cl. Hence the valency of NH_4^+ radical is 1. (iii) Each of SO_4^{--} and CO_3^{--} radicals combines with 2 atoms of hydrogen. Hence these radicals are bivalent. (iv) Similarly PO_4 and BO_3 form H_3PO_4 (orthophosphoric acid) and H_3BO_3(orthoboric acid) respectively. Therefore these two radicals are trivalent. (v) Each of the CrO_4^{--} (Chromate) and $Cr_2O_7^{--}$ (Dichromate) radicals unites with 2 atoms of K, a monovalent metal, to form K_2CrO_4 and $K_2Cr_2O_7$ respectively. Hence both chromate and di-chromate are bivalent.

Again the knowledge of oxidation number concept gives an idea about the valency of the radical. In this method the oxidation number of electropositive element is assumed to be positive (+) and for electronegative element it is negative (−). The algebric sum of the oxidation numbers of all the atoms denotes the valency of the radical e.g., the O.N. of P in PO_4 is +5, O is −2. Hence the O.N. of PO_4 $=(+5)+4(-2) = +5-8 = -3$. Since the O.N. of PO_4 is −3 and it is electronegative radical and it is trivalent. Again the O.N. of N in NH_4 is −3 and that of hydrogen is +1. Hence the O.N. of $NH_4 = -3+4\times1 = -3+4 = +1$. Thus the radical NH_4 is electropositive and its valency is 1.

3.3. Writing of correct formula of compounds.

Classification of elements and radicals in terms of valency has made the study of chemistry much easier. Moreover the formula of a chemical compound can be found out with the knowledge of valency. An ionic compound consists of two parts, a positive part and a negative part. The compound is, as a whole, electrically neutral. Hence the total positive charge contained in the metallic part or basic radical must be equal to the nagative charge contained in the non-metallic part or acid radical.

Let us assume a compound which consists of two elements *M* and *N*. Let their valencies be *x* and *y* respectively. Then the formula of the compound will be M_yN_x i.e., the number of atoms of *M* combining with the number of atoms of *N* to form the molecule of *MN* is in the inverse ratio of the valencies of *M* and *N*. The same rule is applied when two radicals or one element and one radical combine together.

Thus the formula is expressed by writing the valency of *N* on the immediate right and little below of *M* and the valency of *M* is similarly placed by the right of *N*. This method has been illustrated below in finding out the formula of aluminium sulphate. The respective valencies are shown on the right of Al and SO_4.

$$\begin{tikzcd} \mathrm{Al} & 3 \arrow[dl] \\ (\mathrm{SO_4}) & 2 \arrow[ul] \end{tikzcd} \longrightarrow \mathrm{Al_2(SO_4)_3}$$

The above procedure will be more clarified in the following table—

Compound	Valencies of the atom and radicals in the compound	Formula of the compound
Sodium chloride	$\begin{tikzcd} \mathrm{Na} & 1 \arrow[dl] \\ \mathrm{Cl} & 1 \arrow[ul] \end{tikzcd}$	NaCl
Calcium nitride	$\begin{tikzcd} \mathrm{Ca} & 2 \arrow[dl] \\ \mathrm{N} & 3 \arrow[ul] \end{tikzcd}$	Ca_3N_2
Ferric sulphide	$\begin{tikzcd} \mathrm{Fe} & 3 \arrow[dl] \\ \mathrm{S} & 2 \arrow[ul] \end{tikzcd}$	Fe_2S_3
Cuprous sulphate	$\begin{tikzcd} \mathrm{Cu} & 1 \arrow[dl] \\ \mathrm{SO_4} & 2 \arrow[ul] \end{tikzcd}$	Cu_2SO_4

Compound	Valencies of the atom and radicals in the compound	Formula of the compound
Potassium carbonate	$\mathrm{K} \quad 1$ $\mathrm{CO_3} \quad 2$	K_2CO_3
Ammonium sulphate	$\mathrm{NH_4} \quad 1$ $\mathrm{SO_4} \quad 2$	$(NH_4)_2SO_4$
Phosphorous pentoxide	$\mathrm{P} \quad 5$ $\mathrm{O} \quad 2$	P_2O_5
Sodium metaborate	$\mathrm{Na} \quad 1$ $\mathrm{BO_2} \quad 1$	$NaBO_2$
Aluminium oxide	$\mathrm{Al} \quad 3$ $\mathrm{O} \quad 2$	Al_2O_3
Bismuth sulphate	$\mathrm{Bi} \quad 3$ $\mathrm{SO_4} \quad 2$	$Bi_2(SO_4)_3$

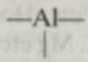
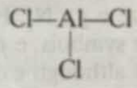
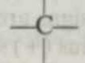
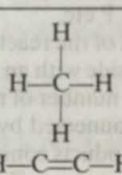
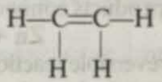
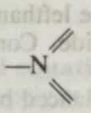
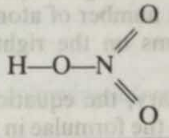
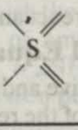
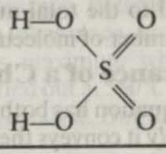
3.4. Structural formula.

The formula so far discussed is the molecular formula of the compound which only indicates the number of atoms of the constituent elements present in the compound. *The arrangement of atoms in a molecule is indicated by structural formula which shows how the atoms in the molecule are linked together by valence bond. Structural formula, in effect, is a 3 dimensional arrangement of atoms in the molecule.* Valence bonds are represented by line or dash or link (—). In writing structural formula the number of valence of an atom is represented by number of hyphen (-) or bonds around the atom. Atoms unite together according to their valencies to form molecule. Hence in a structural formula the bonds of the different atoms are united together. A single bonded atom i.e., atom having monovalency is united with another single bonded atom. Again 2 single bonds of an atom may unite with a double bond of another atom. Similarly 3 single bonds of an atom may unite with a triple bond with a second atom. Since H, Cl etc., atoms are monovalent, they are represented as —H, —Cl. The valencies of O, Ca are 2. Hence they are denoted by —O—, —Ca—. In analogous way nitrogen is $-\underset{|}{\mathrm{N}}-$ and carbon is $-\overset{|}{\underset{|}{\mathrm{C}}}-$

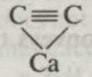
[It must be noted that this pictorial representation of the atoms by hyphen or dash does not imply the real arrangement of atoms in a molecule. The method is used only for the sake of convenience.]

The structural formulae of some of the compounds are shown below :—

Element	Valency	Bond (s) representing the valency	Structural formula of the compound	Formula
N	3	$-\underset{\vert}{\mathrm{N}}-$	$\mathrm{H}-\underset{\underset{\mathrm{H}}{\vert}}{\mathrm{N}}-\mathrm{H}$	NH_3

Element	Valency	Bond (s) representing the valency	Structural formula of the compound	Formula
Al	3			$AlCl_3$
C	4		  $H-C\equiv C-H$	CH_4 C_2H_4 C_2H_2
N	5			HNO_3
S	6			H_2SO_4

Sometimes the determination of valency of an element from the molecular formula of its compound may lead to erroneous result. Structural formula rectifies this error e.g., the formula of calcium carbide is CaC_2. This shows that the valency of Ca is twice the valency of carbon i.e., the valency of Ca is 8 but the structural formula of calcium carbide indicates that Ca is bivalent and carbon is tetra valent.



Similarly in the foumula of carbon suboxide, carbon is apparently divalent and oxygen is trivalent, but its structural formula is $O = C = C = C = O$ which shows the bivalency of oxygen and tetravalency of carbon.

3.5. Chemical equations.

A *chemical reaction* results either from the decomposition of a compound or by the union of atoms or molecules, i.e., by the rearrangement of the compound leading to new products whose properties are different from those of the reacting species. A new bond is formed during the chemical transformation. *The chemical species which participate in the chemical change are called* **reactants** and *the new compounds formed after the change are known as* **products.** A chemical reaction is represented by a chemical equation.

- *A chemical equation is a shorthand representation of a chemical reaction expressing its qualitative and quantitative aspects with the aid of symbols and formulae or a chemical equation is a symbolic expression of a chemical transformation.*

• Method of Writing Chemical Equations :

(i) The reactants and the products are first symbolically represented. Since the atoms of elements cannot exist in the free state, they are to be written in their molecular formula. e.g., N_2, H_2, H_2SO_4 etc. However monoatomic molecules are expressed by their symbols, e.g., Cu, Na, Mg etc.

Some elements although exist in the polymeric form, are usually expressed as monomer, e.g., S, P etc.

(ii) The formula of the reactants are written on the lefthand side and the products on the right hand side with an equal to sign (=) in between them.

(iii) In case, the number of reactants and products is more than one, the formulae of the reactants connected by plus (+) signs are to be written on the left and the formulae of the products connected by plus (+) signs are to be put on the right.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

(iv) In case of reversible reaction, the symbol $\rightleftharpoons$ is used instead of equal to sign (=).

(v) According to the law of conservation of mass, the total mass of the reactants before a chemical change is equal to the total mass of the products after the change. Hence the total number of atoms of the lefthand side is always equal to the total number of atoms on the righthand side. Consequently the equation must be balanced.

(vi) If necessary, the equation is balanced by placing smallest simple integral numbers before the formulae in such a way so that the total number of atoms on the left side is equal to the total number of atoms on the right side. These numbers represent the number of molecules that react and that are produced.

3.6. Significance of a Chemical Equation.

A chemical equation has both qualitative and quantitative significances. Thus :

(i) *Qualitatively* it conveys the names of the reactants which enter into a chemical change and also the products which are formed after the reaction is complete.

(ii) *Quantitatively* it denotes the number of atoms and molecules of reactants and products.

(iii) The chemical equation also signifies *the weights* of the reactants and that of the products.

(iv) In case of a gaseous reaction the equation signifies *the volumes* of the reactants and the products if gaseous.

(v) The chemical equation also conveys the relative *number of* moles of the reactants and products.

Examples : (A) An equation involving solid substances.

$$2Al + 6HCl = 2AlCl_3 + 3H_2$$

The above equation conveys the following informations :—

(i) Aluminium reacts with hydrochloric acid to yield aluminium chloride and hydrogen.

(ii) 2 atoms of aluminium react with 6 molecules of hydrochloric acid to form 2 molecules of aluminium chloride and 3 molecules of hydrogen.

(iii) The total number of atoms of the reactants (2+6+6 = 14) and that of the products (2+6+6 = 14) are the same.

(iv) 2×27 parts by weight of aluminium (At. wt. of Al = 27) react with 6×36·5 parts by weight of HCl to produce 2×27+6×35·5 parts by weight of $AlCl_3$ and 6 parts by weight of H_2.

(v) 2 gram atoms of Al react with 6 gram moles of HCl to produce 2 gram moles of $AlCl_3$ and 3 gram moles of hydrogen.

(vi) 54 g of Al reacts with 219 g of HCl to produce 267 g of $AlCl_3$ and 6 g of H_2.

(B) An equation involving gaseous substances.

$$2H_2 + O_2 = 2H_2O.$$

The above equation conveys the following informations :—

(i) Hydrogen combines with oxygen to form water.

(ii) 2 molecules of hydrogen combine with 1 molecule of oxygen to yield 2 molecules of water.

(iii) The total number of atoms of the reactants (4+2=6) and that of the products (2×2+2=6) are the same.

(iv) 4 parts by weight of hydrogen combine with 32 parts by weight of oxygen to form 36 parts by weight of water.

(v) 2 gram moles of hydrogen combine with 1 gm mole of oxygen to produce 2 gm moles of water.

(vi) Under the same conditions of temperature and pressure 2 vols of H_2 combine with 1 vol of O_2 to form 2 vols of steam.

(vii) At N.T.P. 2×22·4 litres of H_2 combines with 22·4 litres of O_2 to produce 2×22·4 litres of steam.

- **Limitations of a chemical equation :**

A chemical equation does not supply us with the following informations.

(i) **Conditions :** The conditions such as temperature, pressure, presence of a catalyst and other factors under which the reaction takes place, are not known from a chemical equation. The yield of ammonia is maximum when the reaction expressed in the equation $N_2 + 3H_2 = 2NH_3$, is carried out at 550°C under a pressure of 200 atmospheres in presence of iron powder as catalyst. But these informations are not supplied by the chemical equation.

(ii) **Thermal change :** A chemical equation does not provide us about any thermal change which takes place during a chemical reaction i.e., the equation does not tell us whether a reaction is exothermic or endothermic.

Nitrogen combines with hydrogen to form ammonia which takes place with the evolution of 23 k cals of heat. The equation representing this reaction $N_2 + 3H_2 = 2\,NH_3$ does not provide any such information.

(iii) **Time and rate :** The equation does not indicate the rate at which the reactants combine and time of completion of the reaction. Thus the reaction $H_2 + F_2 = 2HF$ is very fast but the reaction $H_2 + I_2 = 2HI$ is very slow. The chemical equations, however, do not give any indication about this.

(iv) **Physical state :** The physical state of the reactants and the products are not indicated by the equation, i.e., whether the reactants and the products are solid or liquid or gaseous.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

Thus, when steam is passed over red hot iron, solid ferrosoferric oxide (Fe_3O_4) is produced with the evolution of hydrogen gas. The chemical equation does not convey this information.

(v) **Density or concentration :** Density or concentrations of the reactants or the products in solution are not provided by the equation.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O \cdots\cdots\cdots\cdots (i)$$
$$4Cu + 10HNO_3 = 4Cu(NO_3)_2 + N_2O + 5H_2O \cdots\cdots\cdots\cdots (ii)$$

In reality, the reaction represented by the equation (i) hot and concentrated HNO_3 is used and by the equation (ii) cold and dilute HNO_3 is used. We cannot predict these simply by observing the equations.

(vi) **Reversibility :** The equation does not indicate, otherwise mentioned, if the reaction is reversible or goes to completion in one direction only. Thé equation $N_2 + 3H_2 = 2NH_3$ is actually a reversible reaction.

(vii) **Mechanism of reaction :** The chemical equation does not indicate the mechanism of reaction, i.e., whether the reaction takes place in one step or in several steps and what are the intermediate transition states, etc.

- **Modern method of writing chemical equation :**

In recent times several symbols are used in the chemical equation to indicate the nature of the raction, physical states of the reactants and products, change of energy, i.e., whether exothermic or endothermic etc. These are explained by taking suitable examples.

(i) *In case of a reversible reaction,* the sign ($\rightleftharpoons$) is used instead of the sign (=). The sign ($\rightleftharpoons$) is known as the sign of reversibility. $N + 3H_2 \rightleftharpoons 2NH_3$

This indicates that the synthesis of ammonia from N_2 and H_2 is a reversible reaction.

(ii) *The physical state of the reactants and the products* are symbolised by (*s*) for solid, (*l*) for liquid and (*g*) gases.

The symbols are placed just after or below the formulae of the reactants and the products.

$$C(s) + O_2(g) = CO_2(g)\ ; \qquad N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(iii) The symbol '(*aq*)' is used to indicate the *aqueous solution of the substance.*

$$CaCO_3(s) + 2HCl(aq) = CaCl_2(aq) + CO_2(g) + H_2O(l)$$
$$Mg(s) + 2HCl(aq) = MgCl_2(aq) + H_2(g)$$

(iv) *If a reaction proceeds with the aid of heat* the symbol $\triangle$ is generally used in between the reactants and the products.

$$2Pb(NO_3)_2(s) \xrightarrow{\triangle} 2PbO(s) + 4NO_2(g) + O_2(g)$$

(vi) *In case of catalytic reaction,* the symbol of the catalyst is used as shown below :

$$4NH_3 + 5O_2 \xrightarrow[700°C]{Pt} 4NO + 6H_2O$$

(vi) *In case of exothermic or endothermic reactions,* the amount of heat evolved or absorbed is written in the equation on the R.H.S. If Q be the the amount of heat evolved, it is written as +Q cals after the products on R.H.S. If, on the other hand, Q be the amount of heat absorbed, it is written as −Q after the products on R.H.S. In thermodynamic sense this change of heat can be symbolised as $\triangle H$ *(Enthalpy or heat of reaction)* $\triangle$ *is −ve for exothermic reaction and +ve for endothermic reaction.*

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22{\cdot}4 \text{ k cals.}$$
$$C(s) + 2S(s) \rightleftharpoons CS_2(l) - 2{\cdot}2 \text{ k cals.}$$
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \triangle H = -22{\cdot}4 \text{ k cals.}$$
$$C(s) + 2S(s) \rightleftharpoons CS_2(s) \quad \triangle H = +2{\cdot}2 \text{ k cals.}$$

(vii) The sign (↓) is placed to the right of a product to denote its precipitation and the sign (↑) is placed to the right of the product to indicate its evolution in gaseous form e.g.,

$$BaCl_2(aq) + H_2SO_4(aq) = BaSO_4\downarrow + 2HCl(aq)$$
$$Mg(s) + 2HCl(aq) = MgCl_2(aq) + H_2\uparrow$$

3.7. Methods of balancing chemical equation.

An unbalanced equation may represent the reaction qualitatively but it does not provide the true information about the reaction. Hence is the necessity of balancing an equation. Five methods are there to balance an equation. These are—

A. Hit and trial method.

B. Partial equation method.
C. Algebric method.
D. Oxidation number method.
E. Ion electron method.

The last two methods will be elaborated in the chapter 'Oxidation and Reduction' in Vol. II. The first 3 methods will be discussed here. Whatever may be the method, the following points are to be always borne in mind while balancing a chemical equation.

(i) The products forming during a reaction.

(ii) The correct molecular formulae of all the reactants and the products.

(iii) The number of molecules of the reactants and the products can never be fractional.

(iv) The total number of atoms of the reactants must be equal to the total number of atoms of the products.

[A] Hit and Trial method :

Simple equations can be balanced by this method. The method involves the following steps :—

(i) Write the molecular formula of the reactants on the L.H.S. and the products on the R.H.S. of the equation. Potassium chlorate when heated yields potassium chloride and oxygen.

$$KClO_3 \rightarrow KCl + O_2$$

(ii) Count the total number of atoms of individual elements on both sides. Mentally balance the atoms on both sides by increasing the number of molecules of the reactants and products so that the number of atoms of each element on both the sides of the equation becomes the same.

Now put the sign (=) in between the reactants and products. It is observed that if two molecules of $KClO_3$ are taken on the L.H.S., 2 molecules of KCl and 3 molecules of O_2 are required on the R.H.S. to balance the equation. Hence the balanced equation will be

$$2KClO_3 = 2KCl + 3O_2$$

(iii) Manganese dioxide reacts with concentrated hydrochloric acid to produce manganous chloride, chlorine and water. This reaction is symbolically represented as $MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$. This is not a balanced equation as the number of chlorine atoms and the number of oxygen atoms on both sides of the equation are not the same. It is observed that if 4 molecules of HCl are taken on the left hand side, the number of chlorine atoms on both the sides becomes equal. It is further observed that in doing this 2 molecules of H_2O are needed on the R.H.S. Hence the balanced equation will be

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

[B] Partial equation method :

As already mentioned, the Hit and Trial method is really tedious and takes a long time particularly when the number of reactants and products are more than two. In order to overcome these difficulties the partial equation method, has been used in balancing a complicated equation. In this method it is assumed that the reaction takes place in several steps. Every step is expressed in the form of a balanced equation called partial equation. The method involves the following steps :—

(a) Write 'partial equation' for each step. Usually the products in the first partial equation becomes reactants in the second partial equation.

(b) Balance each partial equation by hit and trial method.

(c) The balanced equation is finally obtained by adding the partial equations in such a way so that *all* the intermediate products are eliminated.

(d) In order to eliminate the intermediate products sometimes it is necessary to multiply the partial equations by proper integers.

Examples :

(1) When gaseous chlorine is passed through ferrous sulphate solution acidified with dil. sulphuric acid, the products are ferric sulphate and hydrochloric acid.

$$FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + HCl$$

$$\begin{array}{lcccccccccc}
\text{The first partial equation is} & H_2O & & & + & Cl_2 & = & 2HCl & & + & O \\
\text{The second partial equation is} & 2FeSO_4 & + & H_2SO_4 & + & O & = & Fe_2(SO_4)_3 & & + & H_2O \\
\cline{2-11}
\text{On adding} & 2FeSO_4 & + & H_2SO_4 & + & Cl_2 & = & Fe_2(SO_4)_3 & & + & 2HCl
\end{array}$$

Here the individual step is balanced by trial and inspection. The intermediate nascent oxygen is eliminated.

(2) Metallic copper reacts with moderately strong nitric acid to form copper nitrate, water and nitric oxide.

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$$

HNO_3 is believed to split up to produce nascent oxygen which in the second step oxidises copper to cupric oxide. This being a basic oxide reacts with HNO_3, to form salt and water.

$$\begin{array}{l}
2HNO_3 = H_2O + 2NO + 3O \\
3Cu + 3O = 3CuO \\
3CuO + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2O \\
\hline
3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O
\end{array}$$

(3) When H_2S is passed into an acidified solution of potassium permanganate the products are sulphur, potassium sulphate, manganous sulphate and water.

$$KMnO_4 + H_2SO_4 + H_2S \rightarrow K_2SO_4 + MnSO_4 + S + H_2O$$

(i) In the first step $KMnO_4$ is supposed to be decomposed into K_2O, MnO and nascent oxygen. (ii) In the second step the nascent oxygen oxidises H_2S into S and H_2O. (iii) In the following steps the two basic oxides K_2O and MnO separately combine with H_2SO_4 to form salt and water, i.e., potassium sulphate, manganous sulphate and water. The numbers are so chosen that the intermediates, i.e., K_2O, MnO and O are fully cancelled out.

$$\begin{array}{l}
2KMnO_4 = K_2O + 2MnO + 5O \\
5H_2S + 5O = 5S + 5H_2O \\
K_2O + H_2SO_4 = K_2SO_4 + H_2O \\
2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O \\
\hline
5H_2S + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5S + 8H_2O
\end{array}$$

(4) Hydrogen sulphide reacts with an acidified solution of potassium dichromate to produce potassium sulphate, chromic sulphate, sulphur and water.

Like potassium permanganate in the previous equation $K_2Cr_2O_7$ is also supposed to break up into K_2O, Cr_2O_3 and nascent oxygen.

$$\begin{array}{l}
K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O \\
3H_2S + 3O = 3S + 3H_2O \\
K_2O + H_2SO_4 = K_2SO_4 + H_2O \\
Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O \\
\hline
K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O
\end{array}$$

[C] Algebric Method :

In case of complicated reactions, equations can be balanced by algebric method. The method is based on the fact that in the chemical equation the total number of atoms of each element on both L.H.S. and R.H.S. of an equation is equal. The method involves the following steps :—

(i) Assign co-efficients a, b, c, d, e etc. to both the reactants and the products.

(ii) In the next step equate atoms of each kind on both side in terms of the co-efficients.

(iii) Set up simple algebric equation in terms of a, b, c etc. Find their values.

(iv) Substitute the values of a, b, c, d when the equation is balanced.

The technique is illustrated by the following equations—

1. *Reaction between MnO_2 and concentrated HCl leading to the formation of chlorine, manganous chloride and water :—*

$$MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$$

Let the balanced equation be—

$$aMnO_2 + bHCl = cMnCl_2 + dCl_2 + eH_2O$$

Since the number of atoms of all elements are the same on both the sides of the equation, to equalise for the

atoms of Mn : $a = c$
" " O : $2a = e$
" " H : $b = 2e$
" " Cl : $b = 2c + 2d$

Let us now arbitrarily put $a = 1$ then $c = 1$, $e = 2$, $b = 4$

$b = 2c + 2d$ or, $4 = 2 \cdot 1 + 2d$ or, $d = 1$

Substituting the values of the co-efficients, the balanced equation is—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

2. *Reaction between metallic copper and moderately concentrated HNO_3 yields NO, H_2O and $Cu(NO_3)_2$*

Let the balanced equation be—

$$aCu + bHNO_3 = cCu(NO_3)_2 + dNO + eH_2O$$

To equalise for the

atoms of Cu : $a = c$
" " H : $b = 2e$
" " N : $b = 2c + d$
" " O : $3b = 6c + d + e$

Put arbitrarily $b = 1$ Then, $e = \frac{1}{2}$; $d = \frac{1}{4}$ and $a = c = \frac{3}{8}$

or, $\frac{3}{8}Cu + HNO_3 \rightarrow \frac{3}{8}Cu(NO_3)_2 + \frac{1}{4}NO + \frac{1}{2}H_2O$

Multiplying both side by 8

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

3. *Reaction between $K_2Cr_2O_7$ and concentrated HCl :—*

Let the balanced equation be—

$$aK_2Cr_2O_7 + bHCl = cKCl + dCrCl_3 + eCl_2 + fH_2O$$

To equalise for the

atoms of K : $2a = c$
" " Cr : $2a = d$
" " O : $7a = f$
" " H : $b = 2f$

„ „ Cl : $b = c + 3d + 2e$

Putting arbitrarily $a = 1$ then $d = 2, f = 7, e = 2$ and $b = 14$

Again $b = c + 3d + 2e$

$14 = 2 + 6 + 2e$ or, $e = 3$

Substituting the co-efficients in the equation, the balanced equation is

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

3.8. Types of Chemical reactions.

Chemical reaction is an atomic phenomenon. Whenever one or more than one substance undergo chemical reaction, the structure of their molecules undergo transformations leading to new molecules of different orientations. This phenomenon is called chemical reaction.

Chemical reactions are believed to take place by the collisions among the reacting molecules. When the reacting molecules come closer together collision takes place as a result of which the structure of the molecules changes—the result is a chemical reaction. But all molecular collisions are not effective for the chemical change. This is because a large percentage of collisions become ineffective if the colliding molecules are not in proper orientation. Hence in order to have an effective collision leading to chemical transformation, the colliding molecules must not only come closer together but also their orientations must be proper at the time of collision. After these collisions the shape of the molecules changes leading to a new shape. Mechanism of a chemical reaction depends not only on the orientation of the molecules but also on (a) *Concentration of reactants,* (b) *Temperature,* (c) *Presence of a catalyst,* (d) *Pressure of the reaction* (Nuclear reactions are, however, independent of temperature, pressure, catalyst or concentration of the medium).

Thus (i) Red P and iodine or metallic mercury and sulphur are kept in vessel, no noticeable change occurs, but when red P and iodine or mercury and sulphur are ground in a mortar with a pastle immediate reaction takes place.

$$P_4 + 12I_2 = 4PI_3$$
$$Hg + S = HgS$$

(ii) Aluminium powder when boiled with water, the powder dissolves with the evolution of hydrogen but it is a common practice to boil water in Al utensils for years together in our kitchen. This shows that the *reactivity increases with the increase of surface area.*

(iii) The synthesis of SO_3 from SO_2 and O_2 is effected by V_2O_5 (*Vanadium pentoxide*) catalyst.

(iv) *Sound accelerates* the decomposition of mercury fulminate.

(v) Many reactions do not take place at room temperature but do so at high temperature. Thus at room temperature Mg has no action on CO_2 but burning Mg continues to burn in an atmosphere of CO_2 to form black particles of C.

$$2Mg + CO_2 = 2MgO + C$$

(vi) The synthesis of NH_3 from nitrogen and hydrogen takes place at 200 atmosphere. Thus environment i.e., temperature, pressure, catalyst etc., plays a significant role in bringing about the chemical reaction.

Chemical reactions are classified into the following types —

1. **Synthesis :** *When a chemical compound is formed by the direct combination of its constituents the resulting reaction is called synthesis.*

Thus when Mg is burnt in oxygen, the metal directly combines with oxygen to form magnesium oxide. $2Mg + O_2 = 2MgO$

Similarly; $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $2H_2 + O_2 = 2H_2O$, $N_2 + O_2 = 2NO$

2. **Decomposition :** *Decomposition or Analysis is the process of disruption of the molecule of a substance into one or more new substances having new properties.* Truly speaking decomposition is the reverse process of synthesis. Thus when water is electrolysed the molecule of water is decomposed to form hydrogen and oxygen.

$$2H_2O = 2H_2 + O_2$$

3. **Substitution :** *It involves the replacement of one or more atoms of a molecule of a compound by atoms of more active element.* Thus when Fe reacts with $CuSO_4$ the former replaces the Cu atom to form $FeSO_4$.

$$Fe + CuSO_4 = FeSO_4 + Cu$$

4. **Double decomposition or Metathesis :** *When the constituents of the reacting molecule mutually exchange their places and form new compounds, the reaction is called double decomposition or Metathesis.* Thus when a solution of silver nitrate is treated with a solution of potassium iodide a precipitate of silver iodide and potassium nitrate solution are formed.

$$AgNO_3 + KI = KNO_3 + AgI \downarrow$$

5. **Reversible reaction :** *A reaction is said to be reversible when the rate of the forward and backward reaction is the same, i.e., when the products, as soon as are formed, react to reform the reactants. Such reactions are represented by ⇌ sign.*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

6. **Addition reaction :** *Unsaturated compounds react with other reactants directly without loss of any part of the molecules of the reactants. These reactions are called addition reactions. Organic compounds containing double and triple bonds exhibit addition reactions.*

$$C_2H_4 + Cl_2 = C_2H_4Cl_2$$

$$C_2H_4 + O_3 = C_2H_4O_3 \text{ (Ethylene ozonide)}$$

7. **Rearrangement of atoms—isomerisation :** *In this reaction atoms present in the molecule of a compound rearrange themselves to form an altogether new compound due to the change of conditions of the reaction.* The percentage composition of both the reactant and product remains same. Thus ammonium cyanate on being heated is converted to urea.

$$\underset{\text{ammonium cyanate}}{NH_4CNO} \longrightarrow \underset{\text{urea}}{CO(NH_2)_2}$$

8. **Hydrolysis :** *Chemical changes brought out by water is termed as hydrolysis.* As a result of this the products are usually acidic or alkaline. Thus PCl_5 on hydrolysis gives rise to phosphoric acid and HCl.

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

9. **Redox reaction :** *A reaction in which one of the reactants is oxidised and the other is reduced, is called redox reaction.*

oxidised

$$2\overset{+3}{Fe}Cl_3 + \overset{+2}{Sn}Cl_2 = 2\overset{+2}{Fe}Cl_2 + \overset{+4}{Sn}Cl_4$$

reduced

10. **Disproportionation or dismutation reaction :** *In this reaction a particular element in a compound suffers simultaneous oxidation and reduction* i.e., a portion of the element is oxidised by another portion of the same element in a compound. The compound which under goes disproportionation reaction, contains an element in an intermediate oxidation state. The two products obtained from the original compound will be such that in one, the element will be in higher oxidation state and in the other the element will be in lower oxidation state.

oxidised

$$4H_3\overset{+3}{P}O_3 = 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$$

reduced

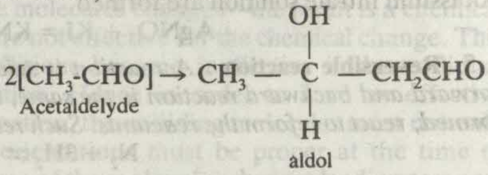
$$2Cu^{+}(aq) = Cu^{++}(aq) + Cu^{0}(s)$$

$$\overset{0}{Cl_2} + 2NaOH = Na\overset{-1}{Cl} + NaO\overset{+1}{Cl} + H_2O$$

This type of reaction is exhibited by those elements which can exist in more than one oxidation state.

11. **Condensation :** *The union of two or more reactants leading to a product accompanied by the loss of either water, HCl etc., is known as condensation reaction.*

$$2H_2SO_4 = \underset{\text{Pyrosulphuric acid}}{H_2S_2O_7} + H_2O\ ;$$



$$\underset{\text{Acetaldelyde}}{2[CH_3\text{-}CHO]} \rightarrow \underset{\text{aldol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CHO}$$

12. **Polymerisation :** *When two or more molecules of the same substance unite together without loss the H_2O, HCl etc., to form a new molecule whose molecular weight is some exact multiple of the reactant, the reaction is known as polymerisation reaction.* The percentage composition and the empirical formula of the reactant and the product remain the same. The starting material is called monomer while the product is known as polymer.

$$\underset{\text{(Ethylene)}}{nC_2H_4} \rightleftharpoons \underset{\text{(Polythene)}}{(C_2H_4)_n} \qquad \underset{\text{(Acetylene)}}{3C_2H_2} \xrightarrow[500°C]{\text{Cu tube}} \underset{\text{(Benzene)}}{C_6H_6}$$

13. **Chain reaction :** *It is the overall reaction occurs in a number of different steps and the product obtained in one step participates in the successive steps. The fission of uranium by the impact of a neutron releasing tremendous energy is a well known example of chain reaction.*

$${}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{56}Ba^{140} + {}_{36}Kr^{93} + 3\,{}_{0}n^{1} + 200\ \text{MeV}$$

If each of these neutrons happens to strike another nucleus of U^{235}, then, in turn, each one of these will generate 3 more neutrons so that the initial neutron in the first step will now produce 9 neutrons. This process goes on.

14. **Comproportionation reactions :** *This is the reverse of disproportionation reaction.* In this reaction, two substances of the same element having different oxidation numbers form a product in which the element has an intermediate oxidation number. Very few reaction of this type is studied e.g.,

$$\overset{2+}{Ag}(aq) + \overset{0}{Ag}(s) \rightarrow 2\overset{+}{Ag}(aq)$$

The above reaction takes place in aqueous solution.

3.9. Chemical Calculations.

(A) Calculations involving weights to weight.

In evaluating chemical calculations the following points are to be remembered.

(a) Write the balanced equation first.

(b) Write the molecular weights of the reactants and products below their formula.

(c) On the basis of the weights from the raction and given data find the weight of the unknown, e.g.,

$$\begin{array}{ccccccccc} CaCO_3 & + & 2HCl & = & CaCl_2 & + & CO_2 & + & H_2O \\ 100\,g & & 73\,g & & 111\,g & & 44\,g & & 18\,g \\ & & & & & & \text{or} & & \\ & & & & & & 22{\cdot}4 \text{ litre} & & \\ & & & & & & \text{at N.T.P.} & & \end{array}$$

(d) Since these weights are relative they hold true whatever units are used. Hence use the same units (g, pound, kg, etc.) for the reactants and the products.

Besides the above, the following points are also important

(i) Density = $\dfrac{\textbf{Mass}}{\textbf{Volume}}$

(ii) In C.G.S. unit specific gravity = Density.

(iii) Weight of 1 ml hydrogen at N.T.P. = 0·000089 g

(iv) 80% purity of a compound means that 80 parts by weight of pure substance is present in 100 parts by weight of the given compound.

(v) In case of gaseous compound the percentage denotes the percentage by volume. In case of liquid, percentage means either the weight of the substance per 100 cc of the liquid or solution or per 100 parts by weight of the liquid or solution.

(vi) Number of moles = $\dfrac{\textbf{Weight of the substance in gram}}{\textbf{Gram molecular weight.}}$

Examples :

1. *How much sulphuric acid is required to dissolve completely 3 g of magnesium carbonate ? Calculate the weight of* CO_2 *liberated which converts sodium hydroxide into sodium carbonate. What is the weight of sodium carbonate formed ?*

Ans : The equation for the reaction is—

$$\begin{array}{ccccccccc} MgCO_3 & + & H_2SO_4 & = & MgSO_4 & + & CO_2 & + & H_2O \\ 24+12+48=84 & & 2+32+64=98 & & & & 12+32=44 & & \end{array}$$

84 g of $MgCO_3$ is dissolved by 98 g of H_2SO_4

$\therefore$ 3 g of $MgCO_3$ is dissolved by $\dfrac{98\times3}{84} = 3{\cdot}5$ g of H_2SO_4

Again 84 g of $MgCO_3$ yield 44 g of CO_2

3 g of $MgCO_3$ yield $\dfrac{44}{84}\times3 = 1{\cdot}571$ g of CO_2

$$\begin{array}{lccccc} \text{Now } CO_2 & + & 2NaOH & = & Na_2CO_3 & + H_2O \\ \quad 44 & & 2\times40=80 & & 106 & \end{array}$$

44 g of CO_2 react with 80 g of NaOH

1·571 g of CO_2 react with $\dfrac{80}{44}\times1{\cdot}571 = 2{\cdot}86$ g of NaOH

Again 80 g of NaOH yield 106 g of Na_2CO_3

2·86 g of NaOH yield $\dfrac{106}{80}\times2{\cdot}86 = 3{\cdot}789$ g of Na_2CO_3

2. *0·5 g of iodine is liberated when potassium iodide reacts with 10 cc dilute* H_2O_2 *solution. Calculate the percentage of* H_2O_2 *in the solution.* *[I = 127]*

Ans : $\underset{34}{H_2O_2} + 2KI = 2KOH + \underset{254}{I_2}$

It is evident from the equation,

254 g of iodine are liberated from 34 g of H_2O_2

0·5 g of iodine are liberated from $\dfrac{34\times0{\cdot}5}{254} = 0{\cdot}0669$ g

Now 10 cc H_2O_2 solution contain 0·0669 g of H_2O_2
100 cc H_2O_2 solution contain 0·669 g of H_2O_2
Hence the percentage of H_2O_2 in the solution = 0·669.

3. *What weight of zinc and sulphuric acid will be required to produce hydrogen that will reduce 8·5 g of copper oxide to metallic copper.* *[Zn = 65, Cu = 63·5]*

Ans : $\underset{65}{Zn} + \underset{98}{H_2SO_4} = ZnSO_4 + \underset{2}{H_2}$

$\underset{79·5}{CuO} + \underset{2}{H_2} = Cu + H_2O$

On the basis of the second equation :—

79·5 g of CuO are reduced by 2 g of hydrogen

8·5 g of CuO are reduced by $\frac{2\times 8·5}{79·5}$ g of hydrogen

Now 2 g of hydrogen are evolved from 65 g of zinc

$\frac{2\times 8·5}{79·5}$ g of hydrogen are evolved from $\frac{65\times 2\times 8·5}{2\times 79·5}$ g of zinc

= 6·95 g of zinc

Again 2 g of hydrogen are evolved from 98 g of H_2SO_4

$\frac{2\times 8·5}{79·5}$ g of hydrogen are evolved from $\frac{98\times 2\times 8·5}{2\times 79·5}$ g of H_2SO_4

= 10·477 g of H_2SO_4

Hence the wt. of Zn = 6·95 g
Hence the wt. of H_2SO_4 = 10·477 g

4. *Calculate the weight of manganese dioxide and hydrochloric acid of 33% strength that will liberate chlorine sufficient to convert 40 g of potassium hydroxide into potassium chloride and potassium chlorate.* *[Mn = 55]*

Ans : $\underset{\substack{55+32\\=87\text{ g}}}{MnO_2} + \underset{\substack{4\times 36·5\\=146\text{ g}}}{4HCl} = MnCl_2 + \underset{\substack{2\times 35·5\\=71\text{ g}}}{Cl_2} + 2H_2O$

$\underset{\substack{6(39+16+1)\\=336\\=112\text{ g}}}{6KOH} + \underset{\substack{3\times 71\\=213\\=71\text{ g}}}{3Cl_2} = 5KCl + KClO_3 + 3H_2O$

From the equations

112 g of KOH react with 71 g of chlorine which are obtained from 87 g of MnO_2 and 146 g of HCl.

Now the weight of MnO_2 for 40 g of KOH = $\frac{87\times 40}{112}$ = 31·07 g

Again the weight of HCl for 40 g of KOH = $\frac{146\times 40}{112}$

Since the strength of HCl = 33%

Wt. of HCl = $\frac{146\times 40}{112}\times\frac{100}{33}$ = 158·01 g

5. *How much $KClO_3$ must be heated to yield as much oxygen as would be obtained from 100 g of HgO.* *[K = 39, Hg = 200]*

Ans : $\underset{432}{2HgO} = 2Hg + \underset{32}{O_2}$

432 g of HgO yield 32 g of O_2

100 g of HgO yield $\frac{32\times 100}{432}$ g of O_2

Again $\underset{245}{2KClO_3} = 2KClO_3 + \underset{96}{3O_2}$

Now 96 g of O_2 are obtained from 245 g of $KClO_3$

$$\frac{32\times100}{432}\text{ g of }O_2\text{ are obtained from }\frac{245}{96}\times\frac{32\times100}{432}\text{ g of }KClO_3$$

$$= 18{\cdot}9\text{ g of }KClO_3$$

6. *How much (a) potassium nitrate and (b) mercuric oxide must be heated to yield as much oxygen as would be obtained from 35 g of $KClO_3$?*

Ans : $\underset{245}{2KClO_3} = 2KCl + \underset{96}{3O_2}$

245 g of $KClO_3$ on heating yield 96 g of O_2

35 g of $KClO_3$ on heating yield $\frac{96\times35}{245} = 13{\cdot}71$ g of O_2

(a) $\underset{202}{2KNO_3} = 2KNO_2 + \underset{32}{O_2}$

32 g of O_2 are obtained from 202 g of KNO_3

13·71 g of O_2 are obtained from $\frac{202\times13{\cdot}71}{32} = 86{\cdot}55$ g of KNO_3

(b) $\underset{432}{2HgO} = 2Hg + \underset{32}{O_2}$

32 g of O_2 are obtained from 432 g of HgO

13·71 g of O_2 are obtained from $\frac{432\times13{\cdot}71}{32} = 185{\cdot}08$ g of HgO

7. *How much weight will be gained or lost when 2 g of each (a) Calcium carbonate, (b) Lead nitrate and (c) Magnesium will be heated in air ?*

Ans : (a) $\underset{100}{CaCO_3} = CaO + \underset{44}{CO_2\uparrow}$

100 g of $CaCO_3$ lose 44 g of CO_2

2 g of $CaCO_3$ lose $\frac{44\times2}{100} = 0{\cdot}88$ g of CO_2

(b) $\underset{662}{2Pb(NO_3)_2} = 2PbO + \underset{184}{4NO_2\uparrow} + \underset{32}{O_2\uparrow}$

662 g of $Pb(NO_3)_2$ decrease (184+32) = 216 g of weight

2 g of $Pb(NO_3)_2$ decrease $\frac{216\times2}{662} = 0{\cdot}65$ g.

Hence the decrease in weight = 0·65 g.

(c) $\underset{2\times24=48}{2Mg} + O_2 = \underset{2(24+16)\,=\,80}{2MgO}$

Increase of weight 80−48=32 g.

48 g of of Mg on being heated in air the increase of weight = 32 g

2 g of of Mg on being heated in air the increase of weight = $\frac{32\times2}{48} = 1{\cdot}33$ g

Increase of weight = 1·33 g

8. *Hydrogen obtained by the reaction of 20 g of magnesium with dilute HCl reacts completely with Cl_2 liberated by the reaction of Conc. HCl and 90·625 g of Pyrolusite. Calculate the percentage of pure MnO_2 in Pyrolusite.* *[Mn = 55]*

Ans : $\underset{\substack{55+32\\=87\text{ g}}}{MnO_2} + 4HCl = MnCl_2 + \underset{\substack{2\times35{\cdot}5\\=71\text{ g}}}{Cl_2} + 2H_2O$

$\underset{24\text{ g}}{Mg} + 2HCl = MgCl_2 + \underset{2\text{ g}}{H_2}$

$\underset{2\text{ g}}{H_2} + \underset{2\times35{\cdot}5\,=\,71\text{ g}}{Cl_2} = 2HCl$

The above 3 equations show that 2 g of H_2 are obtained from 24 g of Mg. Again 2 g of H_2 require 71 g of chlorine which in turn are obtained frm 87 g of MnO_2.

Hence

24 g of Mg are required for 87 g of MnO_2

or, 20 g " " " " " $\frac{87 \times 20}{24} = 72{\cdot}50$ g

or, 90·625 g of Pyrolusite contain 72·50 g of MnO_2

100 g " " " $\frac{72{\cdot}50 \times 100}{90{\cdot}625} = 80$ g

Hence, Pyrolusite contains 80% of pure MnO_2

9. *3·731 g of silver chloride were obtained when excess silver nitrate solution was added to 1·873 g of a mixture of potassium chloride and sodium chloride solution. Calculate the amount of KCl in the mixture.*

Ans : Let the weight of NaCl in the mixture be x g

$\therefore$ Wt of KCl = $(1{\cdot}873 - x)$ g

$$\underset{58{\cdot}5}{NaCl} + AgNO_3 = \underset{143{\cdot}5}{AgCl} \downarrow + NaNO_3$$

58·5 g of NaCl give 143·5 g of AgCl

x g " " " $\frac{143{\cdot}5 \times x}{58{\cdot}5}$ g " "

$= 2{\cdot}453x$ g of AgCl

Again $$\underset{74{\cdot}5}{KCl} + AgNO_3 = \underset{143{\cdot}5}{AgCl} \downarrow + KNO_3$$

74·5 g of KCl give 143·5 g of AgCl

$(1{\cdot}873 - x)$ " " $\frac{143{\cdot}5 \times (1{\cdot}873 - x)}{74.5}$ g of AgCl

$= (3{\cdot}61 - 1{\cdot}926x)$ g of AgCl

According to the problem,

$2{\cdot}453x + 3{\cdot}61 - 1{\cdot}926x = 3{\cdot}731$

or, $x = 0{\cdot}2296$ g

Weight of KCl = $(1{\cdot}873 - 0{\cdot}2296) = 1{\cdot}6434$ g

10. *Haematite contains 50% of iron. Find the percentage of ferric oxide in the ore.*

Ans : The mol. weight of $Fe_2O_3 = 2 \times 56 + 3 \times 16 = 160$

160 parts by weight of Fe_2O_3 contain 2×56 parts by weight of Fe

100 " " " " " " $\frac{2 \times 56 \times 100}{160} = 70$ parts

$\therefore$ the percentage of Fe in $Fe_2O_3 = 70$

Haematite contains 50% Fe

$\therefore$ 50 parts Fe is present in 100 parts of haematite

70 parts Fe is present in $\frac{100 \times 70}{50} = 140$ parts of haematite

Hence the percentage of Fe_2O_3 in the ore = $\frac{100 \times 100}{140} = 71{\cdot}42$ %

11. *One litre of an acidified solution of $KMnO_4$ containing 15·8 g of $KMnO_4$ is decolourised by passing sufficient amount of SO_2. If the SO_2 is produced by roasting of Iron Pyrites (FeS_2), what amount of Pyrites will be required to produce the necessary amount of SO_2 ?* *(I.I.T. Admission test, 1974)*

Ans :
$$\underset{\substack{2[39+55+64]\\=316}}{2KMnO_4} + \underset{\substack{5(32+32)\\=320}}{5SO_2} + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

or, 316 g of $KMnO_4$ ≡ 320 g of SO_2

$$15.8\text{ g} \text{ " } \text{ " } \equiv \frac{320 \times 15{\cdot}8}{316} = 16\text{ g of } SO_2$$

Again
$$\underset{\substack{4(56+64)\\=4\times 120\text{ g}}}{4FeS_2} + 11O_2 = 2Fe_2O_3 + \underset{\substack{8(32+32)\\=8\times 64\text{ g}}}{8SO_2}$$

or, 8 × 64 g of SO_2 are obtained from 4 × 120 g of FeS_2

$$\text{or,}\quad 16\text{ g " " " " "}\quad \frac{4 \times 120 \times 16}{8 \times 64} = 15\text{ g of } FeS_2$$

12. *When a mixture of NaBr and NaCl is repeatedly digested with H_2SO_4, all the halogens are expelled and Na_2SO_4 is formed quantitatively. With a particular mixture, it was found that the weight of Na_2SO_4 obtained was precisely the same as the weight of NaBr - NaCl mixture taken. Calculate the ratio of the weights of NaCl and NaBr in the mixture.* *(I.I.T. Adm Test 1970)*

Ans : Let the weight of NaCl = x g and the weight of NaBr be y g.

∴ The total weight of the mixture = Weight of $Na_2SO_4 = (x + y)$ g

$$\underset{117\text{ g}}{2NaCl} + H_2SO_4 = \underset{142\text{ g}}{Na_2SO_4} + 2HCl$$

117 g of NaCl yield 142 g of $NaSO_4$

$$x \text{ g " " "} \frac{142x}{117} \text{ " "}$$

$$\underset{206\text{ g}}{2NaBr} + H_2SO_4 = \underset{142\text{ g}}{Na_2SO_4} + 2HBr$$

Weight of Na_2SO_4 obtained from y g of NaBr = $\frac{142y}{206}$ g.

The total weight of $Na_2SO_4 = \left(\frac{142x}{117} + \frac{142y}{206}\right)$

According to the problem, $\frac{142x}{117} + \frac{142y}{206} = x + y$

or, $142x \times 206 + 142y \times 117 = 117 \times 206\,(x + y)$

or, $206x\,(142 - 117) = 117y\,(206 - 142)$

or, $206x \times 25 = 117y \times 64$

or, $\frac{x}{y} = \frac{117 \times 64}{206 \times 25} = \frac{29}{20} = \frac{1{\cdot}45}{1}$

or, weights of NaCl :NaBr = 1·45 :1

13. *A mixture of FeO and Fe_3O_4 when heated in air to a constant weight gains 5% in its weight. Find the composition of the intial mixture. [Fe = 56 ; O = 16]* *(I.I.T Adm Test 1978)*

Ans : Let the wt. of the mixture be 100 g and that of FeO = x g

∴ Wt. of $Fe_3O_4 = (100 - x)$ g

Fe_3O_4 is a double oxide of FeO and Fe_2O_3. On heating only FeO is oxidised but the latter is unaffected.

$$\underset{\substack{4(56+16)\\=4\times 72\text{ g}}}{4FeO} + O_2 = \underset{\substack{2(56\times 2+3\times 16)\\=2\times 160\text{ g}}}{2Fe_2O_3}$$

4×72 g of FeO on oxidation give 2×160 g of Fe_2O_3

$$x \text{ g of FeO on oxidation give } \frac{2 \times 160x}{4 \times 72} = \frac{160x}{114} \text{ g of } Fe_2O_3$$

$$4(FeO.Fe_2O_3) + O_2 = 2Fe_2O_3 + 4Fe_2O_3$$

$$\text{or,} \quad \underset{4 \times 232\,g}{4Fe_3O_4} + O_2 = \underset{6 \times 160\,g}{6Fe_2O_3}$$

4×232 g of Fe_3O_4 on oxidation give 6×160 g of Fe_2O_3

$$(100 - x) \text{ g of } Fe_3O_4 \text{ on oxidation give } \frac{6 \times 160\,(100 - x)}{4 \times 232} \text{ g of } Fe_2O_3$$

In accordance with the condition of the problem the weight of the mixture is increased to 105 g.

$$\therefore \frac{160x}{144} + \frac{6 \times 160\,(100 - x)}{4 \times 232} = 105 \quad \text{or,} \quad x = 20{\cdot}25$$

∴ The percentage of FeO = 20·25 and Fe_3O_4 = 100 − 20·25 = 79·75.

14. *150 g of $CaCO_3$ are in one Kg of HCl solution containing 1/10 of its weight of pure acid. How much $CaCO_3$ will remain undissolved ? What weight of CO_2 would be obtained ?*

Ans :
$$\underset{100\,g}{CaCO_3} + \underset{2 \times 36.5\,g}{2HCl} = CaCl_2 + \underset{44\,g}{CO_2} + H_2O$$

wt of HCl taken = 1 Kg = 1000 g. The wt. of pure acid in 1000 g of HCl Soln. = $1000 \times \frac{1}{10} = 100$ g.

73 g HCl dissolve 100 g of $CaCO_3$

$$100 \text{ g HCl} \;\;\text{"}\;\; \frac{100 \times 100}{73} = 136{\cdot}98 \text{ g}$$

∴ wt. of $CaCO_3$ remain undissolved = 150 − 136·98 = 13·02 g.

73 g of HCl give 44 g of CO_2

$$100 \text{ g " " "} \quad \frac{44 \times 100}{73} = 60{\cdot}27 \text{ g.}$$

15. *1·8062 g of a mixture of NaCl and KCl were heated with excess of conc. H_2SO_4, when 2·168 g of sulphate were obtained. Find the percentage of NaCl and KCl in the mixture. [Cl = 35·5, K = 39·3]*

Ans : Let the wt. of NaCl in the mixture be x g

∴ the wt. of KCl = $(1{\cdot}8062 - x)$ g

$$\underset{117\,g}{2NaCl} + H_2SO_4 = \underset{142\,g}{Na_2SO_4} + 2HCl$$

117 g of NaCl yield 142 g of Na_2SO_4

$$x \text{ g of NaCl yield } \frac{142x}{117} \text{ g of } Na_2SO_4$$

$$\text{Again} \quad \underset{149\,g}{2KCl} + H_2SO_4 = \underset{174\,g}{K_2SO_4} + 2HCl$$

$$\text{Hence } (1{\cdot}8062 - x) \text{ g of KCl yield } \frac{174}{149}(1{\cdot}8062 - x) \text{ g of } K_2SO_4$$

According to the problem,

$$\frac{142x}{117} + \frac{174\,(1{\cdot}8062 - x)}{149} = 2{\cdot}168$$

Solving x = 1·28

∴ the wt. of NaCl = 1·28 g

and the wt of KCl = (1·8062 − 1·28) = 0·526 g

$$\% \text{ of NaCl} = \frac{1{\cdot}28 \times 100}{1{\cdot}8062} = 70{\cdot}86\%$$

$$\% \text{ of KCl} = \frac{0{\cdot}526 \times 100}{1{\cdot}8062} = 29{\cdot}12\%$$

16. *1·84 g of a mixture of $CaCO_3$ and $MgCO_3$ are strongly heated till the constant weight becomes 0·96 g. Find the percentage of $CaCO_3$ and $MgCO_3$ in the mixture.* *[Cal B.Sc. (Pt-I) 1971, 76]*

Ans : $\underset{100\,g}{CaCO_3} = \underset{56\,g}{CaO} + CO_2$ $\qquad$ $\underset{84\,g}{MgCO_3} = \underset{40\,g}{MgO} + CO_2$

Let the wt. of $CaCO_3$ in the mixture be x g $\therefore$ the wt. of $MgCO_3$ is $(1{\cdot}84 - x)$ g
From the equation,
100 g of $CaCO_3$ on heating give 56 g of CaO

x g " " " " , $\frac{56x}{100}$ " .

Again
84 g of $MgCO_3$ on heating give 40 g of MgO

$(1{\cdot}84 - x)$ " " " " $\frac{40(1{\cdot}84 - x)}{84}$ MgO

According to the problem $\frac{56x}{100} + \frac{40(1{\cdot}84 - x)}{84} = 0{\cdot}96$

On solving $x = 1$
The weight of $CaCO_3 = 1$ g and the wt. of $MgCO_3$ $(1{\cdot}84 - 1) = 0{\cdot}84$ g

$\therefore$ % of $CaCO_3 = \frac{1 \times 100}{1{\cdot}84} = 54{\cdot}34$

% of $MgCO_3 = 100 - 54{\cdot}34 = 45{\cdot}66$

17. *The hydrogen gas liberated by the action of dilute H_2SO_4 on 13 g of Zn was passed separately over (a) 10 g and (b) 20 g of hot CuO. Find the wt. of residue in each case.* *(W.B.H.S. 1966)*

Ans : $\underset{65\,g}{Zn} + H_2SO_4 = ZnSO_4 + \underset{2\,g}{H_2}$

$\underset{79\,g}{CuO} + \underset{2\,g}{H_2} = \underset{63\,g}{Cu} + H_2O$

65 g of Zn give 2 g of H_2

13 " " " " $\frac{2 \times 13}{65} = 0{\cdot}4$ g of H_2

Again, 2 g of H_2 reduce 79 g of CuO

0.4 g ,, ,, $\frac{79 \times 0.4}{2} = 15{\cdot}8$ g of CuO

Moreover,
79 g of CuO on reduction give 63 g of Cu

15·8 g " " " " " $\frac{63 \times 15{\cdot}8}{79} = 12{\cdot}6$ g of Cu

Case I :—
Thus 0·4 g of H_2, liberated from 13 g of Zn can completely reduce 15·8 g of CuO.
Hence in the first case the whole of 10 g of CuO will be reduced.

10 g of CuO will yield $= \frac{63 \times 10}{79} = 7{\cdot}97$ g of Cu

Case II :—
0·4 g of H_2 can reduce 15·8 g of CuO to form 12·6 g of Cu.
Since the wt. of CuO=20 g hence the unreacted CuO=(20−15·8)=4·2 g

Hence the wt. of residue in the first case=7·97 g of Cu and in the second case

=Unreacted CuO+Cu produced = 4·2 g + 12·6 g = 16·8 g

18. *Igniting MnO_2 in air converts it quantitatively to Mn_3O_4. A sample of pyrolusite is of the following composition $MnO_2 = 80\%$, SiO_2 and other inert constituents = 15%, the rest being water. The sample is ignited in air to constant weight. What is the percentage of Mn in the ignited sample ? (Mn = 54·9)* (*I.I.T. Adm. Test 1978*)

Ans :
$$\begin{array}{lll} 3MnO_2 & = Mn_3O_4 & + O_2 \\ 3(54{\cdot}9+32) & (3\times 54{\cdot}9+64) & \\ =260{\cdot}7\text{ g} & =228{\cdot}7\text{ g} & \end{array}$$

Let the sample taken be 100 g. Out of this 80 g of MnO_2 are oxidised to Mn_3O_4, 15 g of SiO_2 and the other inert materials remain unaffected, while 5 g of water are vapourised.

From the equation,

260·7 g of MnO_2 on oxidation give 228·7 g of Mn_3O_4

80 ,, ,, ,, ,, ,, ,, $\dfrac{228{\cdot}7 \times 80}{260{\cdot}7} = 70{\cdot}2$ g of Mn_3O_4

Amount of unaffected inert sample = 15 g

Hence the total residue = 70·2 + 15 = 85·2 g

70·2 g of Mn_3O_4 contain $\dfrac{3 \times 54{\cdot}9 \times 70{\cdot}2}{228{\cdot}7} = 50{\cdot}55$ g of Mn

Hence the percentage of Mn in the ignited oxide = $\dfrac{50{\cdot}55 \times 100}{85{\cdot}2} = 59{\cdot}33\%$

[B] Chemical calculations involving weights and volumes.

The working out of calculations of problems involving weights and volumes is the same as that adopted for gravimetric composition of a chemical equation in the previous section, e.g.,

$$\begin{array}{lll} 2H_2 & + O_2 & = 2H_2O\text{ (Steam)} \\ 2\times 22{\cdot}4\text{ litre} & 22{\cdot}4\text{ litre} & 2\times 22{\cdot}4\text{ litre} \\ \text{at N.T.P.} & \text{at N.T.P.} & \text{at N.T.P.} \end{array}$$

i.e., 1 volume of a gaseous reactant or product represents 22·4 litre at N.T.P. (Avogadro's Law)

or, 2 vols of H_2, react with 1 vol of O_2, to form 2 vols of steam (under same conditions of temp and pressure)

or, 4 parts by wt. of H_2, react with 32 parts by wt. of O_2, to form 4 + 32 = 36 parts by wt. of H_2O

Again,
$$\begin{array}{llll} S & + O_2 & = & SO_2 \\ 32\text{ g} & 22{\cdot}4\text{ litre} & & 22{\cdot}4\text{ litre} \\ & \text{at N.T.P.} & & \text{at N.T.P.} \\ & \text{or } 32\text{ g} & & \text{or } 64\text{ g} \end{array}$$

This shows that 32 g of sulphur combine with 32 g of oxygen to give 64 g of SO_2. Also 32 g of sulphur require 22·4 litre of oxygen at N.T.P. to give 22·4 litre of SO_2 at N.T.P.

In working out problems of this type the following points are to be borne in mind.

(i) Write down the equation representing the chemical reaction and find the weights of the reactants and products by the usual method.

(ii) The volumes of the gases in the equation are denoted at N.T.P. i.e., temp. = 0°C = 273K and pressure = 1 atoms = 760 mm.

(iii) If the volumes of the gaseous products are not given at N.T.P., find their volumes at N.T.P. from the combined gas laws equation $\dfrac{PV}{T} = \dfrac{P_1V_1}{T_1}$

(iv) 1 gram mole of any gas occupies 22·4 litre at N.T.P.

(v) Mol. wt. of a gas = 2 × Vapour density.

(vi) 1 litre of hydrogen at N.T.P. weighs 0·089 g or, wt. of 1 ml of hydrogen at N.T.P. = 0·000089 g

(vii) Wt. of 1 litre of any gas at N.T.P. = Vapour density of the gas × 0·09 g

19. *A piece of zinc when reacted with 100 g of aqueous solution of HCl liberated 150 ml of hydrogen gas at 15°C and 740 mm pressure. Calculate the percentage of HCl in the solution.*

Ans : Volume of liberated H_2 gas at N.T.P.

$$= \frac{740 \times 150 \times 273}{288 \times 760} = 138\cdot5 \text{ ml}$$

$$\underset{\substack{2 \times 36\cdot5 \\ =73\,\text{g}}}{Zn + 2HCl} = ZnCl_2 + \underset{\substack{22\cdot4 \text{ litre or } 22400 \text{ ml} \\ \text{at N.T.P.}}}{H_2}$$

From the above equation

22400 ml of H_2 at N.T.P. are obtained from 73 g of HCl

138·5 ml of H_2 at N.T.P. are obtained from $\frac{73 \times 138\cdot5}{22400} = 0\cdot451$ g of HCl

Since 100 g of the given aqueous solution of HCl contain 0·451 g of HCl, the percentage of HCl = 0·451

20. *Find the weight of 96·5% pure marble required to prepare 10 litres of CO_2 at* 27°C and 765 mm pressure.

Ans : Let the vol of CO_2 at N.T.P. be V_2 litre

$V_1 = 10$ litre　　$V_2 = ?$

$P_1 = 765$ mm　　$P_2 = 760$ mm

$T_1 = (27 + 273) = 300$K　　$T_2 = 273$K

From the relation $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$V_2 = \frac{765 \times 10 \times 273}{300 \times 760} = 9\cdot16 \text{ litre}$$

$$\underset{100\,\text{g}}{CaCO_3} + 2HCl = CaCl_2 + \underset{\substack{22\cdot4 \text{ litre} \\ \text{at N.T.P.}}}{CO_2} + H_2O$$

22·4 litre of CO_2 at N.T.P. are obtained from 100 g of marble

9·16 litre of CO_2 at N.T.P. are obtained from $\frac{100 \times 9\cdot16}{22\cdot4}$ g of marble

Hence the weight of 96·5% pure marble = $\frac{100 \times 9\cdot16 \times 100}{22\cdot4 \times 96\cdot5} = 42\cdot37$ g

21. *A balloon of 1000 litres capacity is to be filled with hydrogen at 27°C and 750 mm. What is the minimum quantity of Iron required to liberate the necessary amount of hydrogen ? (Fe = 56)*

Ans : Volume of 1000 litres of hydrogen at N.T.P.

$$= \frac{1000 \times 750 \times 273}{300 \times 760} = 898\cdot03 \text{ litre}$$

$$\underset{3 \times 56\,\text{g}}{3Fe} + 4H_2O = Fe_3O_4 + \underset{\substack{4 \times 22\cdot4 \text{ litre} \\ \text{at N.T.P.}}}{4H_2}$$

4 × 22·4 litre of hydrogen at N.T.P. are obtained from 3 × 56 g of Fe

898·03 litre of hydrogen at N.T.P. are obtained from $\frac{3 \times 56 \times 898\cdot03}{4 \times 22\cdot4} = 1683\cdot8$ g of iron

22. *The hydrogen gas obtained by the reaction betwen 10 g of Zinc and cold dilute H_2SO_4 was passed over 50 g of pure dry and hot CuO. Calculate the weight of the residue at the end of the reaction and the volume of gaseous product at 100°C and 760 mm pressure. [Zn = 65]*

Ans : $$\underset{65\,g}{Zn} + H_2SO_4 = ZnSO_4 + \underset{2\,g}{H_2}$$

65 g of Zn produce 2 g of H_2

10 g of Zn produce $\frac{2 \times 10}{65} = \frac{4}{13}$ g of H_2

Again $CuO + H_2 = Cu + H_2O$

Since 2 g of H_2 combine with 16 g of oxygen

$\frac{4}{13}$ g of H_2 combines with $\frac{16 \times 4}{2 \times 13} = 2{\cdot}46$ g of oxygen

This amount of O_2 is obtained from 50 g of CuO

Hence the wt. of CuO left = 50 − 2·46 = 47·54 g

$$\underset{4\,g}{2H_2} + O_2 = \underset{\substack{2 \times 22{\cdot}4\text{ litre}\\ \text{at N.T.P}}}{2H_2O}$$

$\frac{4}{13}$ g of hydrogen yields $\frac{2 \times 22{\cdot}4 \times 4}{4 \times 13}$ litre of steam at N.T.P

$= \frac{2 \times 22{\cdot}4}{13}$ litre of steam at N.T.P.

The vol of this gas at 100°C and 760 mm

$$\frac{V \times 760}{273 + 100} = \frac{2 \times 22{\cdot}4 \times 760}{13 \times 273} \quad \text{or, } V = 4{\cdot}708 \text{ litre}$$

Hence the vol of steam is 4·708 litre.

23. *1 g of a mixture of $CaCO_3$ and $MgCO_3$ on strong heating yields 240 ml of CO_2 at N.T.P. Find the composition of the mixture.* (*Joint Ent. '78*)

Ans : Let the wt. of $CaCO_3$ be x g $\therefore$ the wt. of $MgCO_3 = (1 - x)$ g

$$\underset{100\,g}{CaCO_3} = CaO + \underset{22{\cdot}4\text{ litres at N.T.P.}}{CO_2}$$

100 g of $CaCO_3$ on heating yield 22.4 litres of CO_2 at N.T.P.

x g " " " " " $\frac{22{\cdot}4 \times x}{100}$ litres " "

Again $$\underset{84\,g}{MgCO_3} = MgO + \underset{22{\cdot}4\text{ litres at N.T.P}}{CO_2}$$

84 g of $MgCO_3$ yield 22·4 liters of CO_2 at N.T.P.

$\therefore$ $(1-x)$ " " $\frac{22{\cdot}4\,(1-x)}{84}$ litres " "

According to the problem,

$$\frac{22{\cdot}4\,x}{100} + \frac{22{\cdot}4\,(1-x)}{84} = 240 \text{ ml} = 0{\cdot}24 \text{ litres}$$

On solving $x = 0{\cdot}628$

$\therefore$ wt. of $CaCO_3 = 0{\cdot}628$ g and wt. of $MgCO_3 = (1 - 0{\cdot}628) = 0{\cdot}372$ g

The percentage of $CaCO_3$ in the mixture $= 0{\cdot}628 \times 100 = 62{\cdot}8$

" " $MgCO_3$ " " " $= 0{\cdot}372 \times 100 = 37{\cdot}2$

24. *Calculate the volume of CO_2 at N.T.P. when 10 litres of HCl of 40% strength and specific gravity 1·16 react with 20 kg Na_2CO_3.*

Ans : The specific gravity of HCl is 1·16 i.e. the weight of 1 ml of HCl = 1·16 g

$\therefore$ The weight of 10 litres of HCl = 11·6 kg

From the given data,

100 kg HCl contain 40 kg pure HCl

11·6 kg " " $\frac{40 \times 11{\cdot}6}{100} = 4{\cdot}64$ kg pure HCl

The equation of the reaction,

$$\underset{106\,\text{g}}{Na_2CO_3} + \underset{73\,\text{g}}{2HCl} = 2NaCl + H_2O + \underset{\substack{22400\,\text{ml}\\ \text{at N.T.P.}}}{CO_2}$$

According to the equation, $Na_2CO_3 : HCl = 106 : 73 = 1{\cdot}45 : 1$ but it is given that 20 kg of Na_2CO_3 react with 4·64 kg of HCl.

Hence $Na_2CO_3 : HCl = 20 : 4{\cdot}64$. This ratio being higher than 1·45 : 1, the weight of Na_2CO_3 is large. Therefore the volume of CO_2 can be evaluated from the weight of HCl.

Hence from the equation,

73 g of HCl at N.T.P. give 22400 ml CO_2 at N.T.P.

73 kg " " " " 22400 litres " "

or, 4·64 kg " " " $\dfrac{22400 \times 4{\cdot}64}{73} = 1423{\cdot}78$ litres of CO_2 at N.T.P.

Hence, the vol. of CO_2 at N.T.P. = 1423·78 litres.

25. *Calculate the volume of N_2 at 227°C and normal presure by the decomposition of 5 g of NH_4NO_2.*

Ans : $\underset{1\text{ mole}}{NH_4NO_2} = \underset{1\text{ mole}}{N_2} + 2H_2O$

5 g of $NH_4NO_2 = \dfrac{5}{64}$ moles

Since 1 mole NH_4NO_2 yields 1 mole N_2

$\therefore$ $\dfrac{5}{64}$ " " " $\dfrac{5}{64}$ " "

Vol. of 1 mole N_2 at N.T.P. is 22·4 litres

" " $\dfrac{5}{64}$ " " " " " $\dfrac{22{\cdot}4 \times 5}{64} = 1{\cdot}75$ litres

Let the vol. of N_2 at 760 mm pressure and 227°C be V_1 litres

$$\frac{PV}{T} = \frac{P_1V_1}{T_1} \qquad \frac{760 \times 1{\cdot}75}{273} = \frac{760 \times V_1}{500}$$

or, $V_1 = 3{\cdot}2$ litres.

Hence the vol of $N_2 = 3{\cdot}2$ litres.

26. *3040 ml of a gas mixture at 27°C and 750 mm pressure contain 20% methane, 60% carbon monoxide and 20% hydrogen. What weight of potassium chlorate will be required to liberate, just sufficient oxygen to oxidise completely the gas mixture ?*

Ans : Let the vol of the gas mixture at N.T.P. be V ml

$$V = \frac{750 \times 3040 \times 273}{300 \times 760} = 2730\text{ ml.}$$

According to the problem,

100 ml mixture contain 20 ml methane, 60 ml carbon monoxide and 20 ml hydrogen.

$\therefore$ Vol of methane in 2730 ml mixture $= \dfrac{20 \times 2730}{100} = 546$ ml

$\therefore$ Vol of carbon monoxide in 2730 ml mixture $= \dfrac{60 \times 2730}{100} = 1638$ ml

$\therefore$ Vol of hydrogen in 2730 ml mixture $= \dfrac{20 \times 2730}{100} = 546$ ml

The equation of combustion reactions :—

(i) $\underset{1\text{ vol}}{CH_4} + \underset{2\text{ vol}}{2O_2} = CO_2 + 2H_2O$ (ii) $\underset{2\text{ vol}}{2CO} + \underset{1\text{ vol}}{O_2} = 2CO_2$

(iii) $$\underset{\text{2 vol}}{2H_2} + \underset{\text{1 vol}}{O_2} = 2H_2O$$

From the above equation,

Vol of O_2 required for the oxidation of 546 ml of methane $= 2 \times 546 = 1092$ ml

" " " " " " " 1638 " " CO $= \frac{1638}{2} = 819$ ml

" " " " " " " 546 hydrogen $= \frac{546}{2} = 273$ ml

∴ The total volume of oxygen required at N.T.P.

$= 1092 + 819 + 273 = 2184 \text{ ml} = 2{\cdot}184$ litres

Again, $$\underset{\text{245 g}}{2KClO_3} = 2KCl + \underset{3 \times 22{\cdot}4 \text{ litres at N.T.P.}}{3O_2}$$

$3 \times 22{\cdot}4$ litres of O_2 at N.T.P. are obtained from 245 g of $KClO_3$

$2{\cdot}184$ " " " " " " " $\frac{245 \times 2{\cdot}184}{3 \times 22{\cdot}4} = 7{\cdot}96$ g $KClO_3$

27. *Find the percentage of $KClO_3$ in a sample containing KCl as impurity, 1·555 g of the sample on strong heating yield O_2 just sufficient to oxidise 152 ml acetylene at 27°C and 750 mm pressure.*

Ans : Let the vol of 152 ml of acetylene at N.T.P. be V ml

$$V = \frac{750 \times 152 \times 273}{760 \times 300} = 136{\cdot}5 \text{ ml}$$

As per equation of the reaction,

$$\underset{\text{2 vols}}{2C_2H_2} + \underset{\text{5 vols}}{5O_2} = 4CO_2 + 2H_2O$$

The vol of O_2 required at N.T.P. to oxidise 136·5 ml acetylene $= \frac{5 \times 136{\cdot}5}{2} = 341{\cdot}25$ ml

Again $$\underset{\text{245 g}}{2KClO_3} = 2KCl + \underset{3 \times 22400 \text{ ml at N.T.P.}}{3O_2}$$

3×22400 ml of O_2 at N.T.P. is obtained from 245 g of $KClO_3$

∴ 341·25 ml of O_2 at N.T.P. is obtained from $\frac{245 \times 341{\cdot}25}{3 \times 22400} = 1{\cdot}244$ g of $KClO_3$

Hence 1·555 g of the sample contain 1·224 g pure $KClO_3$

∴ the percentage of $KClO_3 = \frac{1{\cdot}244 \times 100}{1{\cdot}555} = 80$

28. *Oxygen obtained by heating 12·25 g $KClO_3$ is passed over 5 g of hot carbon when carbon is partially oxidised to CO_2. Calculate the volume of this CO_2 at 27°C and 75 cm pressure. Calculate also the amount of carbon remains unoxidised.*

(W.B.H.S. 1963, '66)

Ans : $$\underset{\text{245 g}}{2KClO_3} = 2KCl + \underset{3 \times 22{\cdot}4 \text{ lit at N.T.P.}}{3O_2}$$

245 g of $KClO_3$ produce $3 \times 22{\cdot}4$ litres of O_2 at N.T.P.

12·25 g " " $\frac{3 \times 22{\cdot}4 \times 12{\cdot}25}{245} = 3{\cdot}36$ litres of O_2 at N.T.P.

Again $$\underset{\text{12 g}}{C} + \underset{\substack{\text{22·4 lit} \\ \text{at N.T.P.}}}{O_2} = \underset{\text{22·4 lits at N.T.P.}}{CO_2}$$

∴ The wt of carbon that reacts with 3·36 litres of O_2 at N.T.P. $= \frac{12 \times 3{\cdot}36}{22{\cdot}4}$ g $= 1{\cdot}8$ g

Therefore the unreacted carbon = 5·0 − 1·8 = 3·2 g
At N.T.P. 22·4 litres of O_2 give 22·4 litres of CO_2
„ „ 3·36 „ „ „ 3·36 „ „ „
Let the volume of CO_2 at 27°C and 75 cm pressure be *V* litres

$$\frac{760\times 3\cdot 36}{273}=\frac{750\times V}{300}$$

$$V=\frac{760\times 3\cdot 36\times 300}{750\times 273}=3\cdot 741 \text{ litres}$$

∴ the required volume of CO_2 = 3·741 litres.

29. *112·0 g of pure iron are completely converted into ferric chloride and dissolved in water. How many litres of H_2S gas at N.T.P. will be required to convert this entire amount of $FeCl_3$ into $FeCl_2$? [Fe = 56, Cl = 35·5]* *(H.S. '84)*

Ans : As per the equation,

$$\text{(i)}\quad \underset{\substack{2\times 56\\ =112\,g}}{2Fe} + 3Cl_2 = \underset{\substack{2(56+3\times 35\cdot 5)\\ =325\,g}}{2FeCl_3}$$

$$\text{(ii)}\quad \underset{325\,g}{2FeCl_3} + \underset{\substack{22\cdot 4\text{ litres}\\ \text{at N.T.P.}}}{H_2S} = 2FeCl_2 + 2HCl + S$$

Equation (i) shows that 325 g of $FeCl_3$ g are obtained from 112 g of Iron and equation (ii) indicates that 325 g of $FeCl_3$ are reduced by 22·4 litres of H_2S at N.T.P. Hence the required volume of H_2S = 22·4 litres at N.T.P.

30. *One gram of an alloy of aluminium and magnesium reacts with excess HCl to form $AlCl_3$, $MgCl_2$ and H_2. The evolved hydrogen collected over mercury at 0°C, occupied 1200 ml at 699 mm. What is the composition of the alloy ?*
(I.I.T. Adm Test, 1971)

Ans :

$$\underset{24\,g}{Mg} + 2HCl = MgCl_2 + \underset{\substack{22\cdot 4\text{ litres}\\ \text{at N.T.P.}}}{H_2}$$

$$\underset{\substack{2\times 27\\ =54\,g}}{2Al} + 6HCl = 2AlCl_3 + \underset{\substack{3\times 22\cdot 4\text{ litres}\\ \text{at N.T.P.}}}{3H_2}$$

Let *V* be the vol. of the liberated H_2 at N.T.P.

$$\therefore\ \frac{760\times V}{273}=\frac{699\times 1200}{273} \quad \text{or, } V=1103\cdot 7 \text{ ml}$$

Let the wt of Mg in the alloy be *x* g
∴ Wt of Al in the alloy = (1−*x*) g
From the equation,
24 g of Mg liberate 22400 ml of hydrogen at N.T.P.

x g „ „ „ $\frac{22400}{24}x$ „ „ „

Similarly,
54 g of Al liberate 3×22400 ml H_2 at N.T.P.

(1−*x*) g „ „ „ $\frac{3\times 22400}{54}(1-x)$ „

According to the problem,

$$\frac{22400x}{24}+\frac{3\times 22400}{54}(1-x)=1103\cdot 7$$

or, Solving $x = 0\cdot 4525$
wt of Mg = 0·4525 g and wt of Al = (1−0·4525) = 0·5475 g
% of Mg = 0·4525×100 = 45·25%
% of Al = 0·5475×100 = 54·75%

31. *A 1·00 g sample of $KClO_3$ was heated under such conditions that a part of it decomposed according to the equation*

$$2KClO_3 = 2KCl + 3O_2$$

and the remaining underwent changes according to the equation

$$4KClO_3 = 3KClO_4 + KCl$$

If the amount of oxygen evolved was 146·8 ml at N.T.P., calculate the percentage by weight of $KClO_4$ in the residue. *(I.I.T. Adm Test, '77)*

Ans : As per the first equation,

245 g of $KClO_3$ on decbmposition yield 3×22400 ml O_2 at N.T.P.

$\therefore$ Wt of $KClO_3$ decomposed to produce 146·8 ml O_2 at N.T.P.

$$= \frac{245\times146\cdot8}{3\times22400} = 0\cdot5352\text{ g}$$

Again wt of $KClO_3$ that has decomposed according to eqn. (ii) is $(1-0\cdot5352) = 0\cdot4648$ g

Again from the eqn. (i),

245 g of $KClO_3$ on decomposition yield 149 g of KCl

0·5352 g " " " " $\frac{149\times0\cdot5352}{245}$

Similarly from the eqn. (ii),

$4\times122\cdot5$ g of $KClO_3$ give 74·5 g of KCl

0·4648 " " " " $\frac{74\cdot5\times0\cdot4648}{4\times122\cdot5}$ g of KCl

$$\text{or, the total wt of KCl} = \frac{149\times0\cdot5352}{245} + \frac{74\cdot5\times0\cdot4648}{4\times122\cdot5} = 0\cdot3961\text{ g}$$

Again from the eqn. (ii) wt of $KClO_4$ obtained from 0·4648 g $KClO_3$

$$= \frac{0\cdot4648\times3\times138\cdot5}{4\times122\cdot5} = 0\cdot3941\text{ g}$$

The total wt of the residue i.e., KCl and $KClO_4$ in equation (i) and (ii)

$$= 0\cdot3961 + 0\cdot3941 = 0\cdot7902\text{ g}$$

$$\%\text{ of }KClO_4 = \frac{0\cdot3941}{0\cdot7902}\times100 = 49\cdot87\%$$

32. *Calculate the volume of CO_2 at N.T.P. obtained by the reaction between 3 kg of sodium carbonate with 5 litres hydrochloric acid of 30% strength. The density of HCl = 1·16 g/ml.*

Ans : Weight of 5 litres of HCl = $5000\times1\cdot16 = 5800$ g

100 g of HCl solution contain 30 g of pure HCl

5800 g " " " $\frac{30\times5800}{100} = 1740$ g of HCl

The reaction between HCl and Na_2CO_3 is

$$\underset{106\text{ g}}{Na_2CO_3} + \underset{73\text{ g}}{2HCl} = 2NaCl + \underset{\substack{22\cdot4\text{ litres}\\ \text{at N.T.P.}}}{CO_2} + H_2O$$

The weight of Na_2CO_3 that reacts with 1740 g of HCl

$$= \frac{106\times1740}{73} = 2526\cdot57\text{ g}$$

Thus it is evident that the whole of Na_2CO_3 i.e., 3 kg or 3000 g is not fully decomposed b HCl.

Hence the vol. of CO_2 is not determined from the amount of HCl required.

From the equation,

73 g of HCl liberate 22·4 litres of CO_2 at N.T.P.

1740 g " " $\frac{22\cdot4\times1740}{73} = 533\cdot92$ litres of CO_2

33. *A sample of Ferrous sulphide reacts with dil H_2SO_4 to form H_2S which contains 9% hydrogen by volume. Calculate the percentage of Fe in the sample. [Fe = 56]*

Ans : Since the sample of FeS contains some free metal Fe, hence hydrogen is evolved.

$$\underset{\substack{56+32\\=88\text{ g}}}{FeS} + H_2SO_4 = FeSO_4 + \underset{\substack{22\cdot4\text{ litres}\\\text{at N.T.P.}}}{H_2S}$$

$$\underset{56\text{ g}}{Fe} + H_2SO_4 = FeSO_4 + \underset{22\cdot4\text{ litres N.T.P.}}{H_2}$$

The liberated H_2S contains 9% by vol. of hydrogen hence rest 91% is H_2S.

Now 22·4 litres of H_2S at N.T.P. are obtained from 88 g of FeS

$\therefore$ 91 litres " " " " " $\dfrac{88 \times 91}{22\cdot4}$ "

= 357·5 g of FeS

Again 22·4 litres of H_2S at N.T.P. are obtained from 56 g of Fe

$\therefore$ 9 litres " " " " " " $\dfrac{56 \times 9}{22\cdot4}$ " "

= 22·5 g of Fe.

$\therefore$ The total wt of the contaminated Ferrous sulphide
= wt of pure FeS + wt of Fe = (357·5 + 22·5) g = 380 g.

$\therefore$ The percentage of Fe in the sample of

$$FeS = \frac{22\cdot5 \times 100}{380} = 5\cdot92.$$

• Eudiometry •

Eudiometry deals with the study of chemical reactions in '*gas phase*'. It is used for the determination of the composition of gaseous mixtures and molecular formulae of gases especially hydrocarbons. The apparatus used for measuring changes in the volume of gases during chemical reactions is **Eudiometer.** Both Gay Lusaac's Law of gaseous volume and Avogadro's hypothesis are used in eudiometry.

Eudiometer : An Eudiometer consists of a U-shaped glass tube, one end of which is open and the other contains a glass bulb (fig. 3.1). The bulb is closed with a glass stopper through which are passed two platinum wires. The wires are so close that electric sparks can be generated when current is passed through the wires. The gas mixture inside the Eudiometer is exploded on passing electric sparks and contraction in volume is observed.

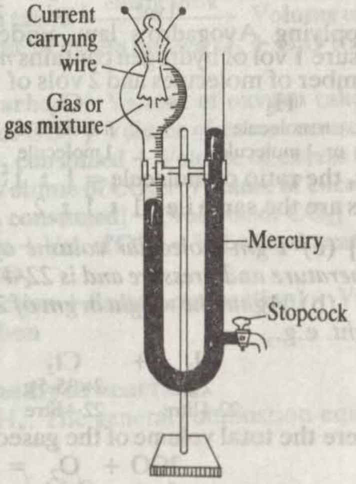


Fig.3.1 : Eudiometer

Principles of Eudiometry :—

At first a known volume of gaseous mixture is introduced through the open end of the tube by the displacement of mercury. The mercury level is made equal on both limbs of Eudiometer by removing Hg through the stop cock. Electric spark is sent through the gas mixture and the reaction starts. After the completion of the reaction, the apparatus is cooled to room temperature when contraction in gaseous volume is observed due to condensation of water vapour. This is known as *first contraction.* This is noted from the graduation

of the limb. Next the residual gas is absorbed by KOH or alkaline pyrogallol. Further contraction in volume is observed. This is called *second contraction* (Fig 3·2).

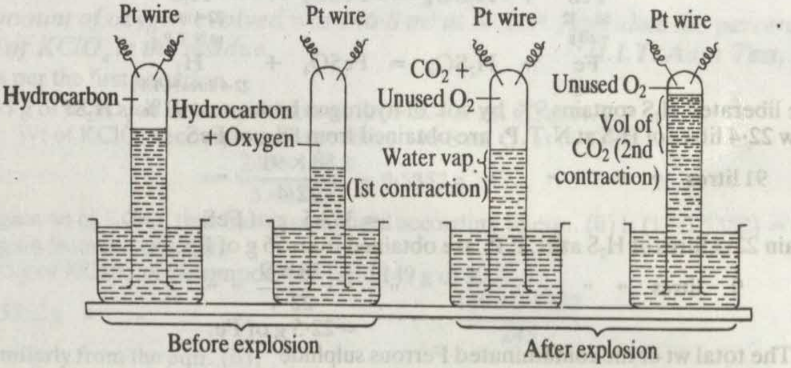


Fig. 3.2 :

If some gases are still left unreacted even after the second contraction, it is noted and calculation regarding the composition of gases or molecular formula of hydrocarbon is made.

• The following points are to be remembered while working problems on Eudiometry :

[1] *The ratio of the volumes and number of molecules of the gaseous reactants and products must be the same.*

Expermentally it has been observed that under the same conditions of temperature and pressure,

$$\underset{1\text{ vol}}{H_2} + \underset{1\text{ vol}}{Cl_2} = \underset{2\text{ vols}}{2HCl}$$

Applying Avogadro's law, under the same conditions of temperature and pressure 1 vol of hydrogen contains *n* number of molecules, 1 vol of chlorine contains *n* number of molecules and 2 vols of HCl will contain 2*n* number of molecules.

$$\underset{\substack{n\text{ molecule}\\ \text{or, 1 molecule}}}{H_2} + \underset{\substack{n\text{ molecule}\\ \text{1 molecule}}}{Cl_2} = \underset{\substack{2n\text{ molecules}\\ \text{2 molecules}}}{2HCl}$$

or, the ratio of molecule = 1 : 1 : 2. Thus the ratio of volume and molecule of gases are the same i.e., 1 : 1 : 2.

[2] (a) *1 gm-molecular volume of all gases is the same under like conditions of temperature and pressure and is 22·4 litre at N.T.P.*

(b) *Again the weight in gm of 22·4 litre of any gas at N.T.P. is its gm-molecular weight.* e.g.,

$$\underset{\substack{2\text{ g}\\ 22\cdot4\text{ litre}}}{H_2} + \underset{\substack{2\times35\cdot5\text{ g}\\ 22\cdot4\text{ litre}}}{Cl_2} = \underset{\substack{2\times36\cdot5\text{ g}\\ 2\times22\cdot4\text{ litre (at N.T.P.)}}}{2HCl}$$

Here the total volume of the gaseous reactant = Total volume of the products.

$$\underset{2\text{ vol}}{2CO} + \underset{1\text{ vol}}{O_2} = \underset{2\text{ vol}}{2CO_2}$$

Before the reaction the total vol = 3 and after reaction = 2.

Hence the contraction in vol = 1.

$$\underset{1\text{ vol}}{CO_2} + C = \underset{2\text{ vol}}{2CO}$$

Here expansion in vol = 1.

The volume of solid and liquid is assumed to be zero.

[3] *An absorbent of common gas is used to absorb a particular gas from the gaseous mixture.*

The volume of gas mixture is measured before and after the use of specific absorbent. The difference indicates the volume of the gas absorbed.

Common gases and their absorbents used in Eudiometry are tabulated.

Gas	**Absorbent**
Oxygen	Alkaline Pyrogallate solution
CO_2 and SO_2	NaOH or KOH solution
CO and C_2H_2	Ammoniacal solution of Cu_2Cl_2
C_2H_4 and NH_3	Conc. H_2SO_4 or Bromine water

[4] *The formula of a gaseous hydrocarbon can be determined by eudiometry.*

(i) If a mixture of known volume of gaseous hydrocarbon and excess of known or unknown volume of oxygen is sparked in Eudiometer, the hydorcarbon is oxidised to CO_2 and H_2O (steam).

$$C + O_2 = CO_2\ ; \qquad 2H_2 + O_2 = 2H_2O$$

(ii) On cooling the apparatus to room temperature, a small contraction in volume due to condensation of water vapour takes place. After cooling, the gas mixture consists of CO_2 and unused excess O_2.

(iii) Now KOH solution is introduced in the tube which absorbs CO_2 completely.

$$2KOH + CO_2 = K_2CO_3 + H_2O$$

As a result, further contraction in volume takes place.

(iv) Now the only gas left in the Eudiometer is unused oxygen. So the second contraction corresponds to the volume of CO_2.

(v) The volume of unused oxygen can be determined by absorbing it with alkaline solution of Pyrogallate.

Thus,

$$\textbf{Volume of hydrocarbon + Volume of oxygen taken} \xrightarrow{\text{electric spark}} \textbf{Volume of } \mathbf{CO_2}$$
$$\textbf{+ Volume of excess unused } \mathbf{O_2} \textbf{ + } \mathbf{H_2O} \text{ (liquid)}$$

Since H_2O is liquid its volume is 0.

∴ First contraction = [Volume of hydorcarbon + Volume of oxygen taken] − [Volume of CO_2 + Volume of excess unused O_2]

= [Volume of hydrocarbon + Volume of O_2 consumed + Volume of excess O_2] − [Volume of CO_2 + Volume of excess O_2]

= [Volume of hydrocarbon + Volume of O_2 consumed] − [Volume of CO_2]

or, **Volume of O_2 consumed = [First contraction + Vol. of CO_2] − Vol. of hydrocarbon.**

Now the Second contraction = Volume of CO_2

or, **Volume of O_2 consumed = [First contraction + Second contraction] − Volume of hydrocarbon**

- **Determination of the formula of the hydrocarbon.**

Let the formula of the hydrocarbon be C_xH_y. The general combustion equation of a hydrocarbon is :—

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 = x\,CO_2 + \frac{y}{2}\,H_2O$$

$$1\text{ vol.} + \left(x + \frac{y}{4}\right)\text{vol.} \quad x\text{ vol.} \quad \frac{y}{2}\text{vol.}$$

(The volume of water is assumed to be zero)

$$\text{First contraction} = \left(1 + x + \frac{y}{4}\right) - x = \left(1 + \frac{y}{4}\right)$$

The values of x and y are evaluated from the experimental and theoretical volumes of CO_2 produced and O_2 consumed.

[5] When the gas mixture exploded in the Eudiometer tube by electric sparks, contraction as well as expansion in volume is mostly observed. In some cases volume does not change at all. Some of the reactions are shown below :

Reactions	**Change of Volume**
1. $2H_2 + O_2 = 2H_2O$ (liquid) 2 vols. 1 vol. = 0 vol.	Contraction = 3 vols. *
2. $2H_2 + O_2 = 2H_2O$ (Steam) 2 vols. 1 vol. = 2 vols.	Contraction = 1 vol.
3. $2CO + O_2 = 2CO_2$ 2 vols. 1 vol. = 2 vols.	Contraction = 1 vol.
4. $2NO + O_2 = 2NO_2$ 2 vols. 1 vol. = 2 vols.	Contraction = 1 vol.
5. $CO_2 + C \rightarrow 2CO$ 1 vol. (Solid) = 2 vols.	Expansion = 1 vol.
6. $N_2 + O_2 = 2NO$ 1 vol. 1 vol. = 2 vols.	No change in vol.
7. $C + O_2 = CO_2$ (Solid) 1 vol. = 1 vol.	No change in vol.

[The combination of free hydrogen and free oxygen leads to the formation of steam which condenses into liquid water. Here 1/3rd of the contraction represents the vol. of O_2 and 2/3rd of the contraction indicates the vol. of H_2 which takes part in the reaction.]

3·10. Numerical problems

[A] Gas Analysis

1. *60 ml of a mixture of N_2O and NO were mixed with equal volume of H_2 gas. On passing electric sparks 38 ml N_2 gas were obtained. Find the composition of the gas mixture.*

Ans : Let the vol. of N_2O be x ml

Hence the vol. of NO = $(60 - x)$ ml.

The effect of explosion is,—

$$\underset{2\text{ vols.}}{2NO} + 2H_2 = \underset{1\text{ vol.}}{N_2} + 2H_2O$$

$$\underset{1\text{ vol.}}{N_2O} + H_2 = \underset{1\text{ vol.}}{N_2} + H_2O$$

1 vol. of N_2O produces 1 vol. of N_2

or, x ml of N_2O produces x ml of N_2

Again 2 vols of NO produce 1 vol of N_2

or, $(60 - x)$ ml of NO produce $\frac{60 - x}{2}$ ml of N_2

But the total vol. of N_2 produced = 38

Hence $x + \frac{60 - x}{2} = 38$ or, $2x + 60 - x = 76$ or, $x = 16$

Hence the composition of the mixture N_2O = 16 ml, NO = 44 ml.

2. *A sample of coal gas contains 40% H_2, 35% CH_4, 15% CO and 10% C_2H_2. 100 ml of this sample of coal gas were mixed with 600 ml air and exploded in an eudiometer. Find out the composition of the residual gas after cooling. Air contains 21% by vol. of O_2.*

Ans : 100 ml of air contain 21 ml of O_2

$\therefore$ 600 " " " " $\dfrac{600 \times 21}{100} = 126$ ml.

Hence the vol. of $N_2 = 600 - 126 = 474$ ml.

The combustion reactions of different contituents :—

$$\begin{array}{llcllcllcl}
\text{(i)} & 2H_2 & + & O_2 & = & 2H_2O\ (l) & & \\
& 2\text{ vols} & & 1\text{ vol} & & & & \\
\text{or,} & 40\text{ ml} & & 20\text{ ml} & & & & \\
\text{(ii)} & CH_4 & + & 2O_2 & = & CO_2 & + & 2H_2O\ (l) \\
& 1\text{ vol} & & 2\text{ vols} & & 1\text{ vol} & & \\
\text{or,} & 35\text{ ml} & & 70\text{ ml} & & 35\text{ ml} & & \\
\text{(iii)} & 2CO & + & O_2 & = & 2CO_2 & & \\
& 2\text{ vols} & & 1\text{ vol} & & 2\text{ vols} & & \\
& 15\text{ ml} & & 7{\cdot}5\text{ ml} & & 15\text{ ml} & & \\
\text{(iv)} & 2C_2H_2 & + & 5O_2 & = & 4CO_2 & + & 2H_2O \\
& 2\text{ vols} & & 5\text{ vols} & & 4\text{ vols} & & \\
& 10\text{ ml} & & 25\text{ ml} & & 20\text{ ml} & &
\end{array}$$

Total vols of O_2 used up $20 + 70 + 7{\cdot}5 + 25 = 122{\cdot}5$ ml.

Unreacted $O_2 = 126 - 122{\cdot}5 = 3{\cdot}5$ ml

Vols of CO_2 produced $= 35 + 15 + 20 = 70$ ml.

Hence the composition of the residual gas mixture—

$O_2 = 3{\cdot}5$ ml. $N_2 = 474$ ml. $CO_2 = 70$ ml.

Total vol $= 547{\cdot}5$ ml.

3. *9·0 ml of a mixture of CH_4 and C_2H_4 is mixed with 30·0 ml of O_2 and the mixture is exploded in an eudiometer tube. On cooling, the resulting gas mixture occupies a volume of 21·0 ml. On shaking the residual gas with KOH, the volume becomes 7·0 ml. Find the volumes of CH_4 and C_2H_4 in the mixture. (All volumes are measured at the same temperature and pressure.)*

Ans : Let the volume of CH_4 be x ml

hence vol of $C_2H_4 = (9 - x)$ ml.

The vol of CO_2 and unreacted O_2 after explosion $= 21$ ml.

CO_2 is completely absorbed by KOH.

Hence the vol of unreacted $O_2 = 7$ ml.

Vol of $CO_2 = (21-7) = 14$ ml.

$\therefore$ Vol of O_2 used up $= 30-7 = 23$ ml.

The combustion reactions are :—

$$\begin{array}{llcllcllcl}
\text{(i)} & CH_4 & + & 2O_2 & = & CO_2 & + & 2H_2O \\
& 1\text{ vol} & & 2\text{ vols} & & 1\text{ vol} & & (l) \\
& x\text{ ml} & & 2x\text{ ml} & & x\text{ ml} & & \\
\text{(ii)} & C_2H_4 & + & 3O_2 & = & 2CO_2 & + & 2H_2O \\
& 1\text{ vol} & & 3\text{ vols} & & 2\text{ vols} & & (l) \\
& (9-x)\text{ ml} & & 3(9-x)\text{ ml} & & 2(9-x)\text{ ml} & &
\end{array}$$

Vol of total CO_2 produced $= x + 2(9-x) = 18-x$ ml.

The vol of CO_2, produced $= 14$ ml.

$\therefore$ $18-x = 14$ or, $x=4$ ml.

Since Vol of CO_2 = Vol of CH_4

or, Vol of $CH_4 = 4$ ml and vol of $C_2H_4 = 9-4 = 5$ ml

Composition : $CH_4=4$ ml and $C_2H_4 = 5$ ml.

4. *1000 ml of a mixture of CO and CO_2 are passed through a red hot coke. After the reaction the volume becomes 1600 ml find the composition of the original mixture. (The vols are measured under the same conditions of temperature and pressure).*

(J.E.E. '80, I.I.T. '80)

Ans : When the gas mixture is passed through red hot coke, CO_2 will be reduced to CO but CO of the mixture will remain unchanged.

$$C + \underset{\text{1 vol}}{CO_2} = \underset{\text{2 vol}}{2CO}$$

Let the vol of CO_2 in the mixture be x ml

∴ Vol of CO = $(1000 - x)$ ml

1 vol of CO_2 produce 2 vols of CO

∴ x ml " " " " $2x$ ml " "

Vol of the mixture after reaction

= Vol of CO formed + Vol of CO in the mixture

= $2x + (1000 - x)$

Given vol after reaction = 1600 ml.

or, $2x + (1000 - x) = 1600$

or, $x = 600$ ml

or, Vol of CO_2 = 600 ml

hence Vol of CO = (1000 − 600) = 400 ml.

Composition of the original mixture 600 ml of CO_2 and 400 ml of CO.

5. *25 ml of Marsh gas at N, T.P. are mixed 300 ml of air at 27 °C and 75 cm pressure and the mixture is exploded in an Eudiometer. Air contains 20% O_2 and 80% N_2 by volume. Calculate the vol. of the residual gas at 17 °C and 75 cm pressure.*

Ans : Let V ml be the vol of the air at N.T.P.

Applying the gas laws equation we get,

$$\frac{300 \times 75}{300} = \frac{V \times 76}{273} \text{ more or, } V = 269{\cdot}4 \text{ ml}$$

$$269{\cdot}4 \text{ ml of air contain } \frac{20 \times 269{\cdot}4}{100} = 53{\cdot}88 \text{ ml } O_2$$

$$\text{and } \frac{80 \times 269{\cdot}4}{100} = 215{\cdot}52 \text{ ml } N_2$$

$$\underset{\substack{\text{1 vol}\\ \text{25 ml}}}{CH_4} + \underset{\substack{\text{2 vol}\\ \text{50 ml}}}{2O_2} = \underset{\substack{\text{1 vol}\\ \text{25ml}}}{CO_2} + 2H_2O\,(l)$$

∴ The composition of the residual gas :—

Nitrogen = 215·52 ml, Oxygen = (53·88 − 50) = 3·88 ml and CO_2 = 25 ml.

The total vol = 215·52 + 3·88 + 25 = 244·40 ml.

$$\frac{244{\cdot}4 \times 76}{273} = \frac{V' \times 75}{290} \text{ or, } V' = 263{\cdot}08 \text{ ml}$$

or, the vol of of residual gas = 263·08 ml.

6. *5 ml H_2O_2 is added to excess of acidified $KMnO_4$ solution. The liberated O_2 is mixed with CH_4 and H_2. The mixture is exploded when a contraction of 43·5 ml is observed. Further contraction of 15·6 ml occurs when it reacts with KOH solution. The residual O_2 is 24·7 ml. Calculate the weight of H_2O_2 per litre. (The volumes of the gases are measured at N.T.P.)*

Ans :

$$\underset{\text{1 vol}}{CH_4} + \underset{\text{2 vols}}{2O_2} = \underset{\text{1 vol}}{CO_2} + 2H_2O\,(l)$$

Vol. of CO_2 formed is $\frac{1}{2}$ the vol. of O_2 consumed. Hence vol. of O_2 required for the generation of $15{\cdot}6$ ml $CO_2 = 2 \times 15{\cdot}6 = 31{\cdot}2$ ml.

From equation,

Contraction in vol = (1 vol + 2 vols) − 1 vol

= 2 vols = vol of O_2 used up.

∴ Contraction of vol. due to formation of $CO_2 = 31{\cdot}2$ ml.

Total contraction in vol = $43{\cdot}5$ ml.

∴ $(43{\cdot}5 - 31{\cdot}2) = 12{\cdot}3$ ml represents vol contraction due to following equation.

$$\underset{2\text{ vols}}{2H_2} + \underset{1\text{ vol}}{O_2} = 2H_2O\,(l)$$

Vol. contraction = 3 vols. The vol. of O_2 which combines with H_2 is $^1/_3$ of this vol.

Hence the vol. of O_2 which combines with $H_2 = \frac{12{\cdot}3}{3} = 4{\cdot}1$ ml

Excess O_2 according to the problem = $24{\cdot}7$ ml.

∴ Total vol of O_2 liberated by the reaction between $KMnO_4$ and $H_2O_2 = 24{\cdot}7 + 4{\cdot}1 + 31{\cdot}2$

= 60 ml. Thus 5 ml of H_2O_2 liberate 60 ml O_2 at N.T.P.

$$2KMnO_4 + 3\,H_2SO_4 + \underset{5\times 34\text{ g}}{5H_2O_2} = K_2SO_4 + 2MnSO_4 + 8H_2O + \underset{5\times 22{\cdot}4\text{ lit. at N.T.P.}}{5O_2}$$

5×22400 ml of O_2 at N.T.P. are liberated from 5×34 g of H_2O_2

60 ” ” ” ” $\frac{5 \times 34 \times 60}{5 \times 22400} = 0{\cdot}091$ g of H_2O_2

Hence the weight of H_2O_2 per litre $= \frac{0{\cdot}091 \times 1000}{5} = 18{\cdot}2$ g

∴ Strength of $H_2O_2 = 18{\cdot}2$ g/lt

7. *60 ml of a mixture of CO and H_2 were mixed with 40 ml O_2 and exploded in an Eudiometer. After cooling, the volume was found to be 30 ml. Find the composition of the original mixture (volumes were measured at the same temperature and pressure).* [*W.B.H.S. '88*]

Ans : Let the vol of H_2 in the mixture be x ml.

∴ Vol of CO in the mixture = $(60 - x)$ ml

The combustion reactions are :—

$$\begin{array}{cccc} 2H_2 & + \quad O_2 & = & 2H_2O\,(l) \\ 2\text{ vols} & 1\text{ vol} & & \\ x\text{ ml} & ^x/_2\text{ ml} & & \\ 2CO & + \quad O_2 & = & 2CO_2 \\ 2\text{ vols} & 1\text{ vol} & & 2\text{ vols} \\ (60-x)\text{ ml} & \frac{(60-x)}{2}\text{ ml} & & (60-x)\text{ ml} \end{array}$$

The residual 30 ml represents the mixture of CO_2 and unreacted O_2.

Total vol of O_2 used up in the combustion

$$= \left(\frac{60-x}{2} + \frac{x}{2}\right)\text{ml} = \frac{60-x+x}{2} = 30\text{ ml}$$

∴ The vol. of unused $O_2 = 40 - 30 = 10$ ml.

After cooling,

Vol of CO_2 formed + Vol of unused O_2 = 30 ml.

or, Vol of CO_2 formed + 10 ml = 30 ml.

or, Vol of CO_2 formed = 30 − 10 = 20 ml.

Now 1 vol of CO produces 1 vol of CO_2

∴ $(60 - x)$ ml ” ” $(60 - x)$ ml of CO_2

Since vol of CO_2 formed = 20 ml.

$\therefore$ 60 − x = 20 or, x = 40 ml.

$\therefore$ The composition of the original mixture : Volume of H_2 = 40 ml, Vol of CO = (60 − 40) = 20 ml.

8. *10 ml of mixture of methane, ethylene and CO_2 were exploded with excess O_2. A contraction of 17 ml was observed after explosion. After the treatment with KOH solution there was a second contraction of 14 ml. Find the percentage of gases in the mixture.*

Ans : Let the vols of CH_4 and C_2H_4 be x and y ml respectively.

$\therefore$ Vol of $CO_2 = \{10 - (x + y)\}$ ml.

Second contraction with KOH = Vol of CO_2 = 14 ml.

The combustion reaction are

$$\text{(i)}\ \underset{\substack{1\text{ vol}\\ x\text{ ml}}}{CH_4} + \underset{\substack{2\text{ vol}\\ 2x\text{ ml}}}{2O_2} = \underset{\substack{1\text{ vol}\\ x\text{ ml}}}{CO_2} + 2H_2O(l)$$

$$\text{(ii)}\ \underset{\substack{1\text{ vol}\\ y\text{ ml}}}{C_2H_4} + \underset{\substack{3\text{ vol}\\ 3y\text{ ml}}}{3O_2} = \underset{\substack{2\text{ vol}\\ 2y\text{ ml}}}{2CO_2} + 2H_2O(l)$$

1st vol contraction = vol of hydrocarbon + vol of O_2 used up − vol of CO_2

$= (x + 2x + y + 3y) - (x + 2y) = 2x + 2y$

or, $2x + 2y = 17$ ………………………………………(1)

Again the total vol. of $CO_2 = x + 2y + 10 - x - y = 14$ or, $y = 4$

Substituting the value of y in eqn. (1)

$2x + 2y = 17$

or, $2x + 2 \times 4 = 17$

or, $2x = 17 - 8 = 9$

or, $x = 4{\cdot}5$

Hence the vol of CH_4 = 4·5 ml

" " C_2H_4 = 4 ml

" " CO_2 = 10 − 8·5 = 1·5 ml

% composition $CH_4 = \dfrac{4{\cdot}5 \times 100}{10} = 45\,\%$

$C_2H_4 = \dfrac{4 \times 100}{10} = 40\,\%$

$CO_2 = \dfrac{1{\cdot}5 \times 100}{10} = 15\,\%$

B : Molecular formula :

9. *20 ml of ammonia gas are exploded in an eudiometer tube. The volume after explosion becomes 40 ml. This volume was mixed with 45 ml of O_2 and is further exploded in the same tube. On cooling, the volume becomes 40 ml. What is the formula of ammonia ?* *(Rajasthan inter '57)*

Ans : (i) On explosion ammonia gives N_2 and H_2

Ammonia → $N_2 + H_2$ = 40 ml.

On mixing 45 ml O_2 the total vol = $N_2 + H_2 + O_2$ = 40 + 45 = 85 ml.

(ii) On second explosion H_2 combines with O_2 to form H_2 and as a result contraction in volume occurs.

$\therefore$ Vol of N_2 + unreacted O_2 = 40 ml.

Vol of H_2 and the O_2 consumed = (85 − 40) = 45 ml

$$\text{Now}\ \underset{2\text{ vol}}{2H_2} + \underset{1\text{ vol}}{O_2} = 2H_2O(l)$$

$\therefore$ Vol of H_2 $= 45 \times \frac{2}{3} = 30$ ml. Vol of $N_2 + H_2 = 40$ ml.

$\therefore$ Vol of N_2 after the 1st explosion $= 40 - 30 = 10$ ml.

Hence it is observed that under the same conditions of temperature and pressure :—
30 ml H_2 + 10 ml N_2 = 20 ml ammonia
Let n be the number of molecules present per vol of gas.
$\therefore$ 30 n molecules of hydrogen + 10 n molecules of nitrogen = 20 n molecules of ammonia.
or, 1 molecule of ammonia contains $\frac{3}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of nitrogen.
Since from Avogadro's hypothesis both nitrogen and hydrogen molecules are diatomic.
1 molecule of ammonia contains 3 atoms of hydrogen and 1 atom of nitrogen.
Hence the formula of ammonia = NH_3

10. *10 ml of a hydrocarbon are mixed with 100 ml O_2 and the mixture is exploded in an eudiometer. On cooling, the volume of the residual gas becomes 95 ml. 20 ml of this are absorbed by KOH solution and the rest by alkaline solution of pyrogallate. What is the formula of the hydrocarbon ?*

Ans : Vol of hydrocarbon = 10 ml.
Vol of oxygen taken = 100 ml.
Vol of CO_2 + unused O_2 = 95 ml
Vol of CO_2 = Vol of gas absorbed by KOH = 20 ml
$\therefore$ Vol of unused $O_2 = 95 - 20 = 75$ ml.
$\therefore$ Vol of O_2 used up for the combustion of the hydrocarbon $= 100 - 75 = 25$ ml.
Let the formula of the hydrocarbon be C_xH_y
The combustion reaction of the hydrocarbon is

$$C_xH_y \quad + \left(x + \frac{y}{4} \right) O_2 \; = \; xCO_2 + \frac{y}{2} H_2O$$

$$1 \text{ mole}, \quad \left(x + \frac{y}{4} \right) \text{mole} \qquad x \text{ mole}$$

$$\text{or, } 1 \text{ vol} \quad \left(x + \frac{y}{4} \right) \text{ vol} \qquad x \text{ vol}$$

$$\text{or, } 10 \text{ ml } 10 \left(x + \frac{y}{4} \right) \text{ ml} \qquad 10x \text{ ml.}$$

According to the problem :— The volume of CO_2 = 20 ml
$\therefore$ $10x = 20$ or, $x = 2$
Again the vol of oxygen consumed = 25 ml

$$\therefore 10 \left(x + \frac{y}{4} \right) = 25$$

$$\text{or, } 10 \left(2 + \frac{y}{4} \right) = 25 \text{ or, } y = 2$$

Hence the formula of the hydrocarbon is C_2H_2 and name Acetylene.

11. *14 ml of a gaseous hydrocarbon were mixed with oxygen and the mixture was exploded. On cooling, there was a contraction of 28 ml. On treatment with KOH solution the volume was further reduced by 14 ml. Calculate the empirical formula of the hydrocarbon. (All volumes were measured at 0°C and 760 mm pressure).*

Ans : Vol of the hydrocarbon = 14 ml
On cooling the 1st contraction = 28 ml
Vol of CO_2 = 14 ml (2nd contraction)
Let the formula of the hydrocarbon be C_xH_y. The balanced equation for its combustion is,

$$C_xH_y \; + \quad \left(x + \frac{y}{4} \right) O_2 = xCO_2 \; + \frac{y}{2} H_2O$$

$$1\text{ vol} \qquad \left(x + \frac{y}{4}\right)\text{ vol} \qquad x\text{ vol}$$

$$14\text{ ml} \qquad 14\left(x + \frac{y}{4}\right)\text{ ml} \qquad 14x\text{ ml}$$

$\therefore 14x = 14$ or, $x = 1$

1st contraction = volume of the reactants − volume of the products

$$= 14\text{ ml} + 14\left(x + \frac{y}{4}\right)\text{ ml} - 14x\text{ ml}$$

$$= 14\text{ ml} + 14x + \frac{7}{2}y - 14x = 14 + \frac{7}{2}y$$

$\therefore 14 + \frac{7}{2}y = 28$ or, $\frac{7y}{2} = 14$

or, $y = \frac{14 \times 2}{7} = 4$

$\therefore$ The empirical formula of the hydrocarbon is CH_4.

12. *A gaseous hydrocarbon requires six times its own volume of O_2 for complete oxidation and produces four times its volume of CO_2. What is its formula ?*

(W.B.H.S. '85)

Ans : Let the formula of the hydrocarbon be C_xH_y

The balanced equation for its combustion is,

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 = xCO_2 + \frac{y}{2}H_2O$$

$$1\text{ vol} \qquad \left(x + \frac{y}{4}\right)\text{ vol} \qquad x\text{ vol}$$

According to the problem, $\left(x + \frac{y}{4}\right) = 6$

or, $4x + y = 24$ ………………(i)

Again $x = 4$ since evolved CO_2 is 4 times that of the hydrocarbon.

Substituting the value of x in (i)

$16 + y = 24$

or, $y = 24 - 16 = 8$

The formula of the hydrocarbon is C_4H_8

13. *0·0225 g of a liquid hydrocarbon was mixed with excess of oxygen and exploded in an eudiometer. On cooling, a contraction of 21 ml was observed (volumes were measured at N.T.P.). The vapour density of the hydrocarbon is 36. Find out its Molecular formula.*

Ans : Since the vapour density of the hydrocarbon is 36, it molecular wt. = 2 × 36 = 72

The volume of 72 g of the hydrocarbon at N.T.P. = 22400 ml

$\therefore$ The volume of 0·0225 g of the hydrocarbon at N.T.P. $= \frac{22400 \times 0{\cdot}0225}{72} = 7$ ml

$\therefore$ The volume of the hydrocarbon taken = 7 ml

Let the formula of the hydrocarbon is C_xH_y

The balanced equation for its combustion is,

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

$$1\text{ vol} \qquad \left(x + \frac{y}{4}\right)\text{ vol} \qquad x\text{ vol}$$

$$7\text{ ml} \qquad 7\left(x + \frac{y}{4}\right)\text{ ml} \qquad 7x\text{ ml}$$

As the hydrocarbon is in liquid state, its volume is neglible.
So the contraction in volume = Vol of hydrocarbon + volume of oxygen − vol of CO_2

$$= 7\left(x + \frac{y}{4}\right) - 7x = \frac{7y}{4}$$

According to the question $\frac{7y}{4} = 21$ or, $y = \frac{21 \times 4}{7} = 12$

The molecular wt. of $C_xH_y = 12x + 1 \times 12 = 12x + 12$.

$\therefore\ 12x + 12 = 72$ or, $12x = 60$ or, $x = 5$

Hence the formula of the required hydrocarbon C_5H_{12}

14. *2·5 litres CO_2 and 3·0 litres water vapour were produced when 500 ml of a gaseous hydrocarbon were mixed with O_2 and exploded in an eudiometer tube. What is the empirical formula of the hydrocarbon ? All volumes were measured under the same conditions of temperature and pressure.* *(I.I.T. '74)*

Ans : Let the formula of the hydrocarbon be C_xH_y
The balanced equation for its combustion is,

$$\begin{array}{llll} C_xH_y + & \left(x + \frac{y}{4}\right)O_2 \rightarrow & xCO_2 + & \frac{y}{2}H_2O \\ 1\ \text{vol} & \left(x + \frac{y}{4}\right)\text{vol} & x\,\text{vol} & \frac{y}{2}\ \text{vol} \\ 500\ \text{ml} & & 500x\ \text{ml} & 500\ \frac{y}{2}\ \text{ml} \end{array}$$

According to the problem $500x = 2500$ or, $x = 5$

Again $500\,\frac{y}{2} = 3000$ or, $y = 12$

Hence the empirical formula of the hydrocarbon = C_5H_{12}

15. *20 ml of a gaseous hydrocarbon are exploded with 66 ml of O_2. The residual gas on cooling is found to occupy 56 ml. On treatment with KOH, the volume is decreased to 16 ml. What is the formula of the hydrocarbon ?* *(J.E.E. '73, '76, '84)*

Ans : Volume of the hydrocarbon = 20 ml
Volume of the oxygen added = 66 ml
Volume of the CO_2 = 56 − 16 = 40 ml
Volume of the unused O_2 = 16 ml
Hence vol of O_2 required to oxidise the hydrocarbon = 66 − 16 = 50 ml
Now

$$\begin{array}{llll} C_xH_y + & \left(x + \frac{y}{4}\right)O_2 \rightarrow & xCO_2 + & \frac{y}{2}H_2O \\ 1\ \text{vol} & \left(x + \frac{y}{4}\right)\text{vol} & x\,\text{vol} & \\ 20\ \text{ml} & 20\left(x + \frac{y}{4}\right)\text{ml} & 20x\ \text{ml} & \end{array}$$

According to the problem $20x = 40$ or, $x = 2$

$$\text{Again}\ \ 20\left(x + \frac{y}{4}\right) = 50$$

$$20\left(2 + \frac{y}{4}\right) = 50 \quad \text{or,}\ y = 2$$

Hence the formula of the hydrocarbon is C_2H_2 or Acetylene.

16. *9 volumes of a gaseous mixture consisting of a gaseous organic compound A and just sufficient amount of O_2 required for complete combustion yielded on burning 4 volumes of CO_2, 6 volumes of water vapour and 2 volumes of N_2, all volumes being*

measured at the same temperature and pressure. If the compound A contained only C, H and N (i) How many volumes of O_2 are required for complete combustion of one volume of A ? (ii) What is the formula of A ? ***(I.I.T. 1974)***

Ans : CO_2 and water vapour are formed from C and H of the hydrocarbon but N remains inert.

4 vols CO_2 require 4 vols oxygen and 6 vols H_2O require half of it, i.e., 6/2 or 3 vols of oxygen. Thus the total vols of O_2 required for the complete oxidation of A = 4 + 3 = 7 vols.

Vol of A in the gas mixture = 9 − 7 = 2 vols.

It is observed thus :—

2 vols of A give 4 vols of CO_2, 6 vols of H_2O and 2 vols of N_2

∴ 1 vol of A gives 2 vols of CO_2, 3 vols of H_2O and 1 vol of N_2

Applying Avogadro's hypothesis

1 molecule of A gives 2 molecules of CO_2, 3 molecules of H_2O and 1 molecule of nitrogen.

or, 1 molecule of A gives 2 atoms of C, 6 atoms of hydrogen and 2 atoms of nitrogen.

Hence the mol. formula of A = $C_2H_6N_2$

$$\begin{array}{lccccccccc}
\text{Again} & A & + & O_2 & \rightarrow & CO_2 & + & H_2O(g) & + & N_2 \\
 & \text{2vols} & & \text{7 vols} & & \text{4 vols} & & \text{6 vols} & & \text{2 vols} \\
\text{or,} & \text{1 vol} & & \frac{7}{2}\ \text{vols} & & \text{2 vols} & & \text{3 vols} & & \text{1 vol.}
\end{array}$$

Thus $\frac{7}{2}$ vols or 3·5 volumes of oxygen are required for the complete combustion of 1 volume of A.

17. *0·9 g of a solid organic compound (Mol wt = 90) containing C, H and O was heated with O_2 corresponding to a volume of 224 ml at S.T.P. After combustion the total volume of the residual gas was 560 ml at S.T.P. On treatment with KOH solution, the volume decreased to 112 ml. Determine the molecular formula of the compound.* *(I.I.T. 1972)*

Ans : Number of moles of the organic compound = $\frac{0{\cdot}9}{90} = 0{\cdot}01$ mole

Vol of CO_2 formed = 560 − 112 = 448 ml at S.T.P.

Mole of CO_2 formed = $\frac{448}{22400} = 0{\cdot}02$ mole

Vol of O_2 taken = 224 ml

Vol of unused O_2 = 112 ml

Vol of O_2 used up = 224 − 112 = 112 ml

Number of moles of O_2 consumed = $\frac{112}{22400} = 0{\cdot}005$ mole

Let the molecular formula of the organic compound = $C_xH_yO_z$

The combustion reaction

$$\begin{array}{lll}
C_xH_yO_z & + \left(x + \frac{y}{4} - \frac{z}{2}\right)O_2 = xCO_2 + \frac{y}{2}H_2O & \\
1\ \text{mole} & \left(x + \frac{y}{4} - \frac{z}{2}\right)\text{mole}\ \ x\ \text{mole} & \\
\text{or, } 0{\cdot}01\ \text{mole} & 0{\cdot}01\left(x + \frac{y}{4} - \frac{z}{2}\right)\text{mole}\ \ 0{\cdot}01x\ \text{mole} &
\end{array}$$

$$\therefore\ 0{\cdot}01\left(x + \frac{y}{4} - \frac{z}{2}\right) = 0{\cdot}005$$

or, $4x + y - 2z = 2$ ················(i)

again, $0{\cdot}01x = 0{\cdot}02$ or, $x = 2$.

Putting value of x, in (i)

$8 + y - 2z = 2$

or, $y - 2z = -6$ ···················(ii)

Now the molecular weight of $C_xH_yO_z = 12x + y + 16z$

or, $12x + y + 16z = 90$
or, $24 + y + 16z = 90$ (substituting $x = 2$)
or, $y + 16z = 66$ ……………………(iii)
From (ii) and (iii) $z = 4$
Substituting the value of z in (ii)
$y - 2\times4 = -6$ or, $y = 2$
Hence the molecular formula of the organic compound = $C_2H_2O_4$

18. *60 ml of a mixture of equal volumes of chlorine and an oxide of chlorine were heated and then cooled back to the original temperature. The resulting gas mixture was found to have a volume of 75 ml. On treatment with KOH solution the volume contracted to 15 ml. Assuming that all measurements were made at the same temperature and pressure, deduce the simplest formula of the oxide of chlorine. (The oxide of chlorine on heating decomposes quantitatively to chlorine and oxygen.)*
(I.I.T. '71)

Ans : Vol of the mixture = 60 ml
Vol of the chlorine = 30 ml
Vol of the oxide of chlorine = 30 ml
Now in accordance with the requirement :

$$\text{Oxide of chlorine} \xrightarrow{\Delta} Cl_2 + O_2$$

Since O_2 is being formed there will be increase in the total volume.
Total vol of the mixture after heating and cooling = 75 ml.
On treatment with KOH the gas absorbed is Cl_2
Absorption = 75 − 15 = 60 ml
Vol of O_2 = 15 ml
Thus 30 ml of the oxide of chlorine contain 15 ml O_2 and 30 ml chlorine
or, 1 ml of the oxide of chlorine contains $\frac{1}{2}$ ml of a oxygen and 1 ml of chlorine.
Applying Avogadro's hypothesis it can be shown that the formula is Cl_2O

19. *10 ml of a gaseous alcohol containing C, H and O only were exploded with 100 ml of pure O_2. On cooling the volume of the residual gas was 90 ml. On treatment with KOH solution, a further contraction in vol of 20 ml was noted. Find the molecular formula and structure of the alcohol if its mol wt is 46.*

Ans : Volume of gaseous alcohol = 10 ml
Volume of O_2 taken = 100 ml
Volume on cooling = 90 ml
Volume of CO_2 = 20 ml
Volume of unused O_2 = 90 − 20 = 70 ml
Hence vol of O_2 used up = 100 − 70 = 30 ml
Let the formula of the alcohol be $C_xH_yO_z$
The combustion reaction

$$C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right)O_2 = xCO_2 + \frac{y}{2}H_2O(l)$$

$$1 \text{ vol} \qquad \left(x + \frac{y}{4} - \frac{z}{2}\right)\text{vol} \qquad x \text{ vol}$$

$$10 \text{ ml} \qquad 10\left(x + \frac{y}{4} - \frac{z}{2}\right)\text{ml} \qquad 10x \text{ ml}$$

Now the vol of CO_2 = 20 ml $\therefore 10x = 20$ or, $x = 2$

$$\text{Again } 10\left(x + \frac{y}{4} - \frac{z}{2}\right) = 30$$

$$\text{or,} \qquad 10\left(2 + \frac{y}{4} - \frac{z}{2}\right) = 30$$

or, $y - 2z = 4$ or, $y = 4 + 2z$

Again Mol wt of $C_xH_yO_z = 12x + y + 16z$

$\therefore\ 12x + y + 16z = 46$

Substitutes the value of x and y

$12 \times 2 + (4 + 2z) + 16z = 46$

or, $18z = 46 - 28 = 18$

or, $z = 1$

Hence the molecular formula of the alcohol = C_2H_6O

It may be CH_3CH_2OH or Ethanol.

20. *A sample of gaseous hydrocarbon occupying 1·12 litres at N.T.P., when completely burnt in air produced 2·2 g of CO_2 and 1·8 g of H_2O. Calculate the weight of the compound taken and the volume of oxygen at N.T.P. required for its burning. Find the molecular formula of the hydrocarbon.* *(I.I.T. '78)*

Ans : Let the formula of the hydrocarbon be C_xH_y

The balanced equation for its burning is,

$$\begin{array}{lllll} C_xH_y + & \left(x + \frac{y}{4}\right)O_2 \rightarrow & xCO_2 + & \frac{y}{2}\,H_2O \\ 1\text{ vol} & \left(x + \frac{y}{4}\right)\text{vol} & x\text{ vol} & \frac{y}{2}\text{ vol} \\ 1\cdot12\text{ lt} & 1\cdot12\left(x + \frac{y}{4}\right)\text{lt} & 1\cdot12x\text{ lt} & 1\cdot12\,\frac{y}{2}\text{ lt} \end{array}$$

Now

$$\text{Volume of } 2\cdot2\text{ g of } CO_2 \text{ at N.T.P.} = \frac{22\cdot4 \times 2\cdot2}{44} = 1\cdot12\text{ lt.}$$

$$\text{Volume of } 1\cdot8\text{ g of } H_2O \text{ (steam) at N.T.P.} = \frac{22\cdot4 \times 1\cdot8}{18} = 2\cdot24\text{ lt.}$$

From the equation weight

$1\cdot12x = 1\cdot12$ or, $x = 1$

and $1\cdot12\,\frac{y}{2} = 2\cdot24$ or, $y = 4$

Hence the molecular formula of the hydrocarbon is CH_4

We know,

At N.T.P. 22·4 lt CH_4 weigh 16 g

$$\therefore\quad 1\cdot12 \text{ ,, ,, ,, } \quad \frac{16 \times 1\cdot12}{22\cdot4} = 0\cdot8\text{ g.}$$

$$\text{Volume of } O_2 \text{ used up} = 1\cdot12\left(x + \frac{y}{4}\right) = 1\cdot12\left(1 + \frac{4}{4}\right) = 2\cdot24\text{ lt at N.T.P.}$$

C. Miscelleneous :

21. *A mixture contains NaCl and an unknown chloride MCl. (i) 1 g of this is dissolved in water. Excess of acidified $AgNO_3$ solution is added to it when 2·567 g of a white precipitate is formed. (ii) 1 g of the original mixture is heated to 300°C. Some vapours come out which are absorbed in an acidified $AgNO_3$ solution, when 1·341 g of white precipitate is obtained. Find the molecular wt. of the unknown chloride.*

[I.I.T. '80]

Ans : Let the mol wt. of MCl = x and the weight of MCl in the mixture = y g.

So the wt. of NaCl = $(1 - y)$ g

(a) $\underset{58\cdot5\text{ g}}{NaCl} + AgNO_3 = NaNO_3 + \underset{143\cdot5\text{ g}}{AgCl}$

(b) $\underset{x\text{ g}}{MCl} + AgNO_3 = MNO_3 + \underset{143\cdot5\text{ g}}{AgCl}$

From equation (a), 58·5 g of NaCl give 143·5 g of AgCl

$$(1-y)\text{ g of NaCl give }\frac{143\cdot5\,(1-y)}{58\cdot5}\text{ g of AgCl}$$

From equation (b), x g of MCl give 143·5 g of AgCl

$$y\text{ g of MCl give }\frac{143\cdot5y}{x}\text{ g of AgCl}$$

$$\text{Total wt. of AgCl formed} = \frac{143\cdot5y}{x} + \frac{143\cdot5\,(1-y)}{58\cdot5}.$$

Given that

$$\frac{143\cdot5y}{x} + \frac{143\cdot5\,(1-y)}{58\cdot5} = 2\cdot567 \ldots\ldots\ldots\ldots (1)$$

From (ii) it is clear that on heating the mixture HCl vapour is given off which forms the precipitate of AgCl. As NaCl can not give HCl on heating the evolved HCl must have come from MCl. So the precipitate of 1·341 g of AgCl is due to MCl only.

$$\underset{x\,\text{g}}{\text{MCl}} \xrightarrow[\Delta]{} \text{HCl} \xrightarrow{\text{AgNO}_3} \underset{143\cdot5\,\text{g}}{\text{AgCl}\downarrow}$$

$$\therefore \text{ The wt. of AgCl obtained from } y \text{ g of MCl} = \frac{143\cdot5y}{x}\text{ g}$$

$$\therefore \frac{143\cdot5y}{x} = 1\cdot341 \ldots\ldots\ldots \text{(2) substituting this value in (1)}$$

$$\text{We get } 1\cdot341 + \frac{143\cdot5\,(1-y)}{58\cdot5} = 2\cdot567$$

Solving $y = 0\cdot5$ g. Substituting the value of y in (2) $\frac{143\cdot5 \times 0\cdot5}{x} = 1\cdot341$ or, $x = 53\cdot5$

The mol. wt. of MCl = 53·5.

22. *1 g of Mg is burnt in a closed vessel which contains 0·5 g of O_2. (i) Which reactant is left in excess ? (ii) Find the weight of the excess reactant. (iii) How many millilitres of 0·5 N H_2SO_4 will dissolve the residue in the vessel ?* *[I.I.T. '80]*

Ans : $\underset{48\,\text{g}}{2\text{Mg}} + \underset{32\text{g}}{\text{O}_2} = \underset{80\text{g}}{2\text{MgO}}$

(i) 48 g of Mg react with 32 g of O_2

$$1\text{ g of Mg reacts with }\frac{32}{48} = 0\cdot66\text{ g of O}_2$$

but only 0·5 g of O_2 is available, hence whole of Mg will not burn, a part will remain as unreacted. So Mg will remain in excess.

(ii) 32 g of O_2 react with 48 g of Mg

$$0\cdot5\text{ g of O}_2\text{ reacts with }\frac{48 \times 0\cdot5}{32} = 0\cdot75\text{ g of Mg}$$

$\therefore$ Wt. of Mg left unreacted = (1 − 0·75) = 0·25 g.

(iii) H_2SO_4 will react with MgO and unreacted Mg.

$$\text{Mg} + \text{H}_2\text{SO}_4 = \text{MgSO}_4 + \text{H}_2$$
$$\text{MgO} + \text{H}_2\text{SO}_4 = \text{MgSO}_4 + \text{H}_2\text{O}$$

H_2SO_4 will react only with Mg atom and the total amount of Mg in the residue (Mg + MgO) is 1 g.

We know, 1 gram eq of $H_2SO_4 \equiv$ 1 gram eq of Mg

or, 1000 ml of (N) H_2SO_4 $\equiv$ 12 g (1 gm-eq) of Mg

$$\begin{aligned}\therefore 1\text{ g of Mg} &\equiv \frac{1000}{12}\text{ ml of (N) H}_2\text{SO}_4\\ &\equiv 83\cdot3\text{ ml of (N) H}_2\text{SO}_4\\ &\equiv \frac{83\cdot3}{0\cdot5}\text{ ml of }0\cdot5\text{ (N) H}_2\text{SO}_4\\ &\equiv 166\cdot6\text{ ml of }0\cdot5\text{ (N) H}_2\text{SO}_4\end{aligned}$$

Hence 166·6 ml of 0·5 (N) H_2SO_4 will be required to dissolve the residue.

23. *A solid mixture (5 g) consisting of lead nitrate and sodium nitrate was heated below 600 °C until the weight of the residue was constant. If the loss in weight was 28 percent, find the amount of lead nitrate and $NaNO_3$ in the mixture.* *[I.I.T. '90]*

Ans : Let the wt. of $NaNO_3$ in the mixture x g.

So the wt. of $Pb(NO_3)_2 = (5 - x)$ g

$NaNO_3$ and $Pb(NO_3)_2$ will decompose as shown in the equation on heating,

$$\begin{array}{ccccccc} 2Pb(NO_3)_2 & = & 2PbO & + & 4NO_2 & + & O_2 \\ 662\,g & & & & 184\,g & & 32\,g \\ & & & & \multicolumn{3}{c}{184+32 = 216\,g} \end{array}$$

$$\begin{array}{ccccc} 2NaNO_3 & = & 2NaNO_2 & + & O_2 \\ 170\,g & & & & 32\,g \end{array}$$

170 g $NaNO_3$ on heating gives 32 g of O_2

x g of $NaNO_3$ on heating gives $\frac{32x}{170}$ g of O_2

662 g of $Pb(NO_3)_2$ give 216 g of gases

$(5 - x)$ g of $Pb(NO_3)_2$ give $\frac{216(5-x)}{662}$ g of gases

Loss of heating the mixture is 28% of 5 g of the mixture $= \frac{28 \times 5}{100} = 1{\cdot}4$ g

$\therefore\ \frac{216(5-x)}{662} + \frac{32x}{170} = 1{\cdot}4$

or, $1{\cdot}63 - 0{\cdot}326x + 0{\cdot}188x = 1{\cdot}4$

or, $0{\cdot}138x = 0{\cdot}23$

or, $x = 1{\cdot}666$

$\therefore$ Wt. of $NaNO_3 = 1{\cdot}666$ g

Wt. of $Pb(NO_3)_2 = 5 - 1{\cdot}674 = 3{\cdot}334$ g

• Emperical formula and molecular formula :

(1) Emperical formula : *The emperical formula of a compound is the simplest formula which expresses the simple whole number ratio of the atoms of different elements present in the molecule.*

It does not indicate the actual number of atoms of each element present in the molecule of the compound.

Calculation of emperical formula.

(i) The percentage of each element present in the compound is determined by actual experiment.

(ii) The percentage of each element is divided by its atomic weight. This gives the relative number of different kinds of atoms present in the molecule.

(iii) The numbers obtained in step (ii) are then divided by the smallest of these numbers H.C.F. so as to give a simple atomic ratio.

(iv) The figures expressing the simple atomic ratio as obtained in step (iii) give the relative number of atoms of each element in the molecule—the minor fractions are neglected as due to experimental error. If necessary, they are further reduced to whole numbers by multiplying with a suitable factor.

The simple atomic ratio thus obtained gives the emperical formula of the compound.

Example : Percentage composition of a compound as determined by analysis was found to be carbon 14·5, hydrogen 1·8, chlorine 64·46, oxygen 19·24. Its emperical formula is to be calculated.

Step I. The percentage composition of each element is divided by its respective atomic weight.

Carbon — 14·5/12 = 1·21, Hydrogen — 1·8/1 = 1·8, Chlorine — 64·46/35·5 = 1·81, Oxygen – 19·24/16 = 1·2.

Step II. These numbers are divided by the smallest number (in this case 1·2). C—1·2/1·2 = 1, H—1·8/1·2 = 1·5, Cl—1·81/1·2 = 1·5, O—1·2/1·2 = 1.

Setp III. By multiplying each with smallest whole number, C—1 × 2 = 2, H—1·5 × 2 = 3, Cl—1 5 × 2 = 3, O—1 × 2 = 2.

Hence the emperical formula of the compound is $C_2H_3Cl_3O_2$.

(2) **Molecular formula :** *The molecular formula of a compound expresses the actual number of atoms of each element present in its molecule.*

It may be the same as that of its emperical formula or on exact multiple of it.

The emperical and molecular formulae are related to each other as follows—

Molecular formula = (emperical formula) n. Where n is a simple integer.

When $n = 1$

Molecular formula = emperical formula.

$$\text{Thus } n = \frac{\text{molecular wt.}}{\text{emperical formula wt.}}$$

Thus the value of n can easily be found out by dividing the molecular wt. by its emperical formula weight. Thus when the emperical formula is multiplied by n, it gives the molecular formula.

- **Numerical examples :**

1. *Calculate the percentage of Al, SO_4 and water of crystallisation in potash alum.* [*W.B.H.S. '65*]

Ans : Formula of potash alum K_2SO_4, $Al_2(SO_4)_3$, 24 H_2O

Molecular wt. of potas alum.

$= (2 \times 39) + 32 + (4 \times 16) + (2 \times 27) + 3\,(32 + 4 \times 16) + 24\,(2 + 16) = 948.$

$$\therefore \text{ percentage of Al} = \frac{54 \times 100}{948} = 5{\cdot}69\%$$

$$\text{percentage of } SO_4 = \frac{384 \times 100}{948} = 40{\cdot}51\%$$

$$\text{percentage of water of crystallisation} = \frac{432 \times 100}{948} = 45{\cdot}57\%$$

2. *Percentage composition of an organic solution as determined by analysis was, Carbon 40%, Hydrogen 6·67% and Oxygen 53·33%. Its vapour density is found to be 2·813 times that of oxygen. Calculate its molecular formula.* [*W.B.H.S. '91*]

Ans :

Element	Percentage	At. Wt.	Ratio of the no. of atoms	Simple atomic ratio
Carbon	40	12	40/12 = 3·33	3·33/3·33 = 1
Hydrogen	6·67	1	6·67/1 = 6·67	6·67/3·33 = 2
Oxygen	53·33	16	53·33/16 = 3·33	3·33/3·33 = 1

∴ The emperical formula of the compound is $C_1H_2O_1$. Let the molecular formula ot the compound is $(CH_2O)_n$ where n is whole number. Its vapour density (H = 1) = 16 × 2·813 = 45. Mol wt = 45 × 2 = 90.

∴ $12n + 2n + 16n = 90$ or, $n = 3$

The molecular formula of the compound is $(CH_2O)_3 = (C_3H_6O_3)$.

3. *1·367 g of a compound consisting of carbon, hydrogen and oxygen. On burning in air yields 3·002 g of CO_2, and 1·64 g of H_2O. Find out the emperical formula of the compound.* [*I.I.T. '75*]

Ans : Molecular wt. of CO_2 = 44.

44 g of CO_2 contain 12 g of carbon

$$3{\cdot}002\text{ g } CO_2 \text{ contain } \frac{12 \times 3{\cdot}002}{44} \text{ g of cabon.}$$

∴ 1·367 g of the compound contain $\frac{12 \times 3\cdot002}{44}$ g of C.

100 g of the compound contain $\frac{12 \times 3\cdot002 \times 100}{44 \times 1\cdot367} = 59\cdot89$ g of C.

Mol wt. of H_2O = 18.

18 g of H_2O contains 2 g of H_2

1·64 g of H_2O contains $\frac{1\cdot64 \times 2}{18}$ g of H_2

∴ 1·367 g of the compound contain $\frac{1\cdot64 \times 2}{18}$ g of H_2

100 g of the compound contain $\frac{1\cdot64 \times 2 \times 100}{18 \times 1\cdot367} = 13\cdot33$ g of H_2.

∴ The percentage of O_2 in the compound = 100 − (59·89 + 13·33) = 26·78.

Element	Percentage	At. Wt.	Ratio of the no. of atoms	Simple atomic ratio
Carbon	59·89	12	59·89/12 = 4·99	4·99/1·67 = 3
Hydrogen	13·33	1	13·33/1 = 13·33	13·33/1·67 = 8
Oxygen	26·78	16	26·78/16 = 1·67	1·67/1·67 = 1

∴ The emperical formula is $C_3\,H_8\,O$

4. *The ratio of the weights of C, H and N in a compound containing carbon hydrogen and nitrogen is 9 : 1 : 3·5. Find its emperical formula. If the molecular wt. of the compound is 108, find its molecular formula.* [*I.I.T. '73*]

Ans :

Element	Ratio of weights	At. Wt.	Ratio of no. of atoms	Simple ratio of atoms
C	9	12	9/12 = 0·75	0·75 × 4 = 3
H	1	1	1/1 = 1	1 × 4 = 4
N	3·5	14	3·5/14 = 0·25	0·25 × 4 = 1

∴ the emperical formula of the compound is $C_3\,H_4\,N$.

Let the molecular formula of the compound be $(C_3H_4N)_n$ where *n* is a whole number.

∴ mol. wt. of the compound = $3 \times 12n + 4 \times 1n + 14n = 54n$.

given that mol. wt. = 108.

∴ $54n = 108$ or, $n = 2$

∴ the molecular wt. = $(C_3H_4N)_2 = C_6H_8N_2$.

5. *Carbon and hydrogen combine together to form three hydrocarbons A, B and C. The percentage of H in A, B and C are 25%, 14·3% and 7·7% respectively. Find the emperical formula of A, B and C.* [*I.I.T. '73*]

Ans :

Compound	P.C. of H and C	Ratio of no. of atom	Simple ratio of atoms	Emperical formula of compound
A	H = 25 C = 75	25/1 = 25 75/12 = 6·25	25/6·25 = 4 6·25/6·25 = 1	CH_4
B	H = 14·3 C = 85·7	14·3/1 = 14·3 85·7/12 = 7·14	14·3/7·14 = 2 7·14/7·14 = 1	CH_2
C	H = 7·7 C = 92·3	7·7/1 = 7·7 92·3/12 = 7·7	7·7/7·7 = 1 7·7/7·7 = 1	CH

6. *0·2 g of an organic compound contain 40·67% of carbon, 8·47% of hydrogen. 37·96 ml of nitrogen are obtained at N.T.P. from the same amount of the compound. Find out the emperical formula of the compound.* [*Bombay Inter.* '77]

Ans : The wt. of 22400 ml of N_2 at N.T.P. is 28 g.

The wt. of 37·96 ml of N_2 at N.T.P. is $\frac{28 \times 37·96}{22400}$ g

∴ the percentage of $N_2 = \frac{28 \times 37·96}{22400} \times \frac{100}{0·2} = 23·72$

the p.c. of Carbon = 40·67, p.c. of H = 8·47 and p.c. of N_2 = 23·72.

∴ the p.c. of O_2 = 100 − (40·67 + 8·47 + 23·72) = 27·14.

Element	Percentage	At. wt.	Ratio of no of atoms	Simple ratio of atoms
C	40·67	12	40·67/12 = 3·34	3·34/1·7 = 2
H	8·47	1	8·47/1 = 8·47	8·47/1·7 = 5
N	23·72	14	23·72/14 = 1·7	1·7/1·7 = 1
O	27·14	16	27·14/16 = 1·7	1·7/1·7 = 1

The emperical formula of the compound is C_2H_5NO.

7. *0·22 g of a sample of a volatile compound containing C, H and Cl only, yielded on combustion in oxygen 0·195 g of CO_2 and 0·0804 g of H_2O. 0·12 g of the compound occupied a volume of 37·24 ml at 105 °C and 768 mm Hg pressure. Calculate the molecular formula of the compound.* [*I.I.T.* '78]

Ans : On combustion in O_2 all carbon and hydrogen atoms of the compound are converted into CO_2 and water respectively.

44 g of CO_2 contain 12 g of carbon

0·195 g CO_2 contain $\frac{12 \times 0·195}{44}$ g of C = 0·0531 g of C

18 g of H_2O contain 2 g of H_2

0·0804 g H_2O contain $\frac{2 \times 0·0804}{18}$ g of H_2 = 0·0089 g of H_2

Hence 0·22 g of the compound contains 0·0531 g of C and 0·0089 g of H_2 and the rest i.e., 0·158 g of Cl_2.

∴ The percentage of C, H and Cl in the compound are —

$$C = \frac{0·0531 \times 100}{0·22} = 24·13\%, \quad H = \frac{0·0089 \times 100}{0·22} = 4·04\%, \quad Cl = \frac{0·158 \times 100}{0·22} = 71·8\%.$$

Let the volume of 0·12 g of the compound occupies V ml at N.T.P. then —

$$\frac{V \times 760}{273} = \frac{37·24 \times 768}{378} \quad \text{or,} \quad V = \frac{273 \times 37·24 \times 768}{378 \times 760} \text{ ml}$$

At N.T.P. $\frac{273 \times 37·24 \times 768}{378 \times 760}$ ml of the compound weighs 0·12 g

∴ At N.T.P. 22400 ml of the compound weighs $\frac{378 \times 760 \times 0·12 \times 22400}{273 \times 37·24 \times 768} = 98·90$ g

∴ The mol. wt. of the compound is 98·90.

Element	p.c.	At. Wt.	Ratio of No. of atoms	Simple ratio of atoms
C	24·13	12	24·13/12 = 2·02	2·02/2·02 = 1
H	4·04	1	4·04/1 = 4·04	4·04/2·02 = 2
Cl	71·8	35·5	71·8/35·5 = 2·02	2·02/2·02 = 1

∴ The emperical formula is CH_2Cl

Let the molecular formula is $(CH_2Cl)_n$, n is a whole number.

∴ Mol. wt. = $12n + 2n + 35·5n = 49·5n$.

$\therefore$ $49{\cdot}5n = 98{\cdot}90$ or, $n = 2$

$\therefore$ The molecular formula of the compound is $C_2H_4Cl_2$.

8. *An organic compound $C_xH_{2y}O_y$ was burnt with twice the amount of O_2 needed for complete combustion to CO_2 and H_2O. The hot gases when cooled to 0°C and 1 atm. pressure, measured 2·24 litres. The water collected during cooling weighed 0·9 g. The vapour pressure of pure water at 20°C is 17·5 mm Hg and is lowered by 0·104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the compound.* *[I.I.T. '83]*

Ans : The combustion reaction of the organic compound can be represented as

$$\underset{1\text{ mole}}{C_xH_{2y}O_y} + \underset{x\text{ mole}}{xO_2} \rightarrow \underset{x\text{ mole}}{xCO_2} + \underset{y\text{ mole}}{yH_2O}$$

0·9 g of water = 0·9/18 = 0·05 moles of water.

Now from equation we get—

y mole of H_2O is obtained from 1 mole of the compound

$\therefore$ 0·05 mole of H_2O is obtained from $\frac{0{\cdot}05}{y}$ mole of the compound

Again from equation,

1 mole of the compound on combustion yielded $x \times 22{\cdot}4$ litre of CO_2

$\therefore$ $\frac{0{\cdot}05}{y}$ of the compound on combustion yields $\frac{x \times 22{\cdot}4 \times 0{\cdot}05}{y}$ litre of CO_2

$= \frac{1{\cdot}12x}{y}$ *litre of CO_2 at N.T.P.*

Since twice the amount of O_2, needed for complete combustion of the compound was used, the residual gas mixture after cooling contains equal volume of O_2 and CO_2. (As required vol. of O_2 for complete combustion of C gives equal vol. of CO_2) Hence the mixture contain 2·24/2 = 1·12 litres of CO_2.

$\therefore$ $\frac{1{\cdot}12x}{y} = 1{\cdot}12$ or, $x/y = 1$ or, $x = y$

$\therefore$ The molecular formula of the compound is $(CH_2O)_x$.

The mol. wt. is $(12+2+16)_x = 30x$.

Now from Raoult's law—

$\frac{\Delta P}{P_0} = \frac{n}{N}$ where, P_0 = vapour pressure of pure solvent, ΔP = vapour pressure lowered, n = moles of solute, N = moles of solvent.

$\therefore$ $\frac{0{\cdot}104}{17{\cdot}5} = \frac{50/M}{1000/18}$ M = molecular wt. of the compound.

$\therefore$ $M = \frac{50 \times 18 \times 17{\cdot}5}{1000 \times 0{\cdot}104} \approx 151$

$\therefore$ $30x = 151$ or, $x \approx 5$

$\therefore$ The molecular formula of the compound is $C_5H_{10}O_5$.

8. *An aromatic compound contains 69·4% C and 5·8% H and 13·25% of O. A sample of 0·303 g of this compound was analysed for N_2 by Kjeldahal's method. The NH_3 evolved was absorbed in 50 ml of 0·05 (M) H_2SO_4. The excess acid required 25 ml of 0·1 (M) NaOH for neutralisation. Determine the molecular formula of the compound if its molecular wt. is 121.* *[I.I.T. '82]*

Ans : As 1(M) H_2SO_4 = 2(N) H_2SO_4, 0·05 (M) H_2SO_4 = 2 × 0·05 (N) H_2SO_4

The amount of NH_3 evolved $\equiv (50 \times 0{\cdot}05 \times 2 - 25 \times 0{\cdot}1)$ ml of (N) H_2SO_4

$\equiv$ 2·5 ml of 1(N) H_2SO_4

1 ml of (N) $H_2SO_4 \equiv$ 0·017 g of $NH_3 \equiv$ 0·014 g of nitrogen

$\therefore$ 2·5 ml of (N) $H_2SO_4 \equiv 2{\cdot}5 \times 0{\cdot}014$ g $\equiv$ 0·035 of nitrogen

0·303 g of the compound contains 0·035 g of N_2

∴ The p.c of N_2 in the compound = $\frac{0·035\times100}{0·303} = 11·55\%$

∴ C : H : O : N ratio of the compound is

$$\frac{69·4}{12} : \frac{5·8}{1} : \frac{13·25}{16} : \frac{11·55}{14} = 5·78 : 5·78 : 5·8 : 0·828 = 7 : 7 : 1 : 1$$

∴ The emperical formula is C_7H_7ON. Since the mol. wt. = 121

∴ $(7\times12+7+16+14)_n = 121$.

or, $n = 1$.

∴ The mol. formula is C_7H_7NO.

9. *A hydrocarbon contains 10·5g of carbon per gram of hydrogen. 1 litre of the hydrocarbon at 127°C and 1 atoms. pressure weighs 2·8g. Find the molecular formula.* *[I.I.T' 83]*

Ans : In the hydrocarbon, 10·5g of carbon contains 1g of hydrogen

∴ 12g of carbon contains 12/10·5 = 1·43g of H_2

∴ The emperical formula of hydrocarbon is $(CH_{1·143})_n$ or, $(C_7H_8)_n$ (multiplying by 7)

Let the volume of the hydrocarbon at NTP be V litres, then $\frac{1\times1}{400} = \frac{V\times1}{273}$ or, $V = \frac{273}{400}$ litres

Now $\frac{273}{400}$ litres of hydrocarbon at N.T.P. weighs 2·8g

∴ 22·4 litres of hydrocarbon at N.T.P. weighs $\frac{2·8\times22·2\times400}{273}$ g = 91·9g

So the Mol. wt of the hydrocarbon is 91·9

∴ $12\times7n + 8n = 91·9$

or, $n = 1$

∴ the molecular formula of the hydrocarbon is C_7H_8

10. *The general formula of carbohydrate is $C_x(H_2O)_y$. 3·1 g of the carbohydrate on heating in absence of O_2 yields 1·24 g of carbon. The molecular weight of the carbohydrate is 180. Calculate its molecular formula.*

Ans : The percentage of C in the carbohydrate is $\frac{1·24\times100}{3·1} = 40$

The percentage of $H_2O = (100-40) = 60$

∴ $C : H_2O = \frac{40}{12} : \frac{60}{18} = 1 : 1$

∴ the emperical formula of the carbohydrate is $C(H_2O)$.

Let the molecular formula is $[C(H_2O)]_n$ where n is a whole number,

∴ $[C(H_2O)]_n = 180$

or, $12n + 2n + 16n = 180$

or, $n = 6$,

∴ the molecular formula is $C_6H_{12}O_6$.

• Exercises •

1. What is a chemical equation ? What informations regarding a chemical reaction can you get from a chemical equation ?

2. What informations regarding the chemical reactions can you get from the following equations ? [W.B.H.S. '71]

(i) $N_2 + 3H_2 = 2NH_3$
(ii) $CaCO_3 = CaO + CO_2$
(iii) $PbS + 4H_2O_2 = PbSO_4 + 4H_2O$
(iv) $2CO + O_2 = 2CO_2$

3. What are the limitations of a chemical equation ? 'The limitations of the chemical equations have not been eliminated mostly'—give suitable examples in support of the above statement.

4. What is meant by balancing a chemical equation ? Why is it essential to balance a chemical equation ?

5. 'A chemical equation does not supply us with all the informations about a chemical reaction'—Justify the statement.

6. State with balanced equation what happens when—(a) Tin is treated with conc. HNO_3, (b) Silver is treated with conc. H_2SO_4, (c) Aluminium is reacted with hot and conc. NaOH soln., (d) Ammonium di chromate is heated, (e) Hydrogen sulphide is passed through a solution of potassium permanganate acidified with sulphuric acid. [*I.I.T.* '79]

7. Complete and balance the following equations :

(i) Copper reacts with HNO_3 to give NO and NO_2 in molar ratio of 2 : 1.

$$Cu + HNO_3 \rightarrow — + NO + NO_2 + —$$

(ii) $CuSO_4 + Na_2CO_3 + H_2O \rightarrow — + Na_2SO_4 + —$
(iii) $P + I_2 + H_2O \rightarrow — + —$
(iv) $KNO_3 + K \rightarrow — + —$
(v) $K_2Cr_2O_7 + HCl \rightarrow KCl + — + — + H_2O$ [*I.I.T.* '92]

8. Complete and balance the following equations :
(a) $KNO_3 + FeSO_4 + H_2SO_4$ (conc.) =
(b) $H_2S + K_2Cr_2O_7 + H_2SO_4 =$
(c) $Mg_3N_2 + H_2O =$
(d) $Al + KMnO_4 + H_2SO_4 =$ [*I.I.T.* '80]

9. Complete and balance the following equations :
(i) $FeSO_4 + HNO_3 + H_2SO_4 \rightarrow — + NO + H_2O$
(ii) $P + HNO_3 + — \rightarrow H_3PO_4 + NO + NO_2$
(iii) $KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + — + —$
(iv) $CuO + NH_3 \rightarrow Cu + — + H_2O$
(v) $Al + NaOH + — \rightarrow — + H_2$
(vi) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + N_2O + —$
(vii) $KMnO_4 + HCl \rightarrow KCl + — + — + H_2O$
(viii) $HNO_3 + SO_2 \rightarrow H_2SO_4 + —$
(ix) $NH_3 + NaOCl \rightarrow — + — + —$
(x) $AgBr + Na_2S_2O_3 \rightarrow — + —$ [*I.I.T.* '93]

10. (a) State the valency of nitrogen in the following compounds— N_2O_2, NO, N_2O_5, NO_2, N_2O_3, N_2. [*I.I.T.* '69]

(b) Give the valency of
(i) S in Na_2SO_4, (ii) Cl in $KClO_3$, (iii) Cr in $K_2Cr_2O_7$, (iv) I in ICl_3, (v) P in H_3PO_4. [*I.I.T.* '70]

11. Name a metal and a non metal having variable valency. Write the formula of their oxides and chlorides.

12. Justify the statements—
(a) A chemical reactions obeys the law of conservations of mass.
(b) The emperical formula of two different compounds may be the same.

13. Explain the following reactions with an example for each (i) Disproportionation reactions, (ii) Re-arrangement reactions. [*WBJEE* '92]

14. Define emperical formula and molecular formula. [*W.B.H.S.* '87]. Mention the differences between emperical and molecular formula. Under what condition do the emperical and molecular formula become same ?

15. Explain the following giving suitable examples (i) synthesis reaction, (ii) substitution reaction. [*W.B.H.S.(T)* '84]

16. Give the structural formula for the following (a) phosphorus acid, (b) Pyrophosphoric acid. [*I.I.T.* '81]

17. Complete and balance the following—
(i) $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$
(ii) $Cr_2O_7^{2-} + C_2H_4O \rightarrow C_2H_4O_2 + Cr^{2+}$
(iii) $HNO_3 + HCl \rightarrow NO + Cl_2$
(iv) $Cl_2 + OH^- \rightarrow Cl^- + ClO^-$

18. Complete and balance the equations :
(i) $[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \rightarrow — + [Fe(H_2O)_6]^{3+}$
(ii) $[Fe(H_2O)_6]^{2+} + — \rightarrow — + H_2O$ [*I.I.T.* '93]

• Numerical problems :

1. What amount of hydrogen peroxide will be liberated when 80 g of H_2SO_4 is reacted on 150 g of barium peroxide ? [***Ans.*** 27·755 g]

2. What amount of Zn will be required to produce H_2 by its action on dil. H_2SO_4, which will completely react with the oxygen, produced by heating 30 g of $KClO_3$? [***Ans.*** 47·75g]

3. 12 g of mixture of $KClO_3$ and KCl on being heated strongly yields 8·08 g of KCl as residue. Find out the percentage of $KClO_3$ in the mixture. [*Ans.* 83·3%]

4. A sample of marble is contaminated with silica. 3 g of this sample is reacted with 6 g of H_2SO_4. After the reaction, it is found that the amount of the unreacted acid is 3·15 g. Find the percentage of pure marble in the sample. [*Ans.* 97%]

5. 10% of sample of sodium nitrate contains an impurity which is inert to H_2SO_4. The sample is reacted with 98% H_2SO_4 by weight. Calculate the amount of the sample and H_2SO_4 required to produce 10 kg of nitric acid. [*Ans.* $NaNO_3$ = 14·99 kg, H_2SO_4 = 7·936 kg]

6. A solution containing 3 moles of KOH is added to a solution containing 2 moles of phosphoric acid. Water is evaporated. What is the composition of the crystals precipitated ?
[*Ans.* 1 mole KH_2PO_4 and 1 mole K_2HPO_4] [*WBJEE '91*]

7. 5·36 g of a mixture of anhydrous sodium carbonate and sodium bi-carbonate lose 1·24 g in weight on heating. Calculate the amount of sodium carbonate and sodium bi-carbonate in the mixture. The residue is dissolved in water and $BaCl_2$ solution is added when a white precipitate is obtained. Find the weight of the precipitate thus obtained. [*Ans.* Na_2CO_3 = 2 g, $NaHCO_3$ = 3·36 g, $BaCO_3$ = 7·67 g]

8. A mixture of formic acid and oxalic acid is heated with conc. H_2SO_4. The gas produced is collected and on its treatment with KOH solution the volume of the gas decreases by 1/6 th. Calculate the molar ratio of the two acids in the original mixture. [*Ans.* 4 : 1] [*Roorke Eng. '90*]

9. What weight of AgCl will be precipitated when a solution containing 4·77 g of NaCl is added to a solution of 5·77 g of $AgNO_3$? [*Ans.* 4·87 g] [*I.I.T. '78*]

10. Crude calcium carbide is made in electric furnace by the following reaction— $CaO + 3C \rightarrow CaC_2 + CO$. The product contains 85% CaC_2 and 5% unreacted CaO. (i) How much CaO is to be added to the furnace charge for each 1000 kg of pure CaC_2 ? (ii) How much CaO is to be added to the furnace charge for each 1000 kg of crude product. [*Ans.* 1051·4 kg, 893·75 kg] [*I.I.T. '67*]

11. 2·68 g of a mixture of $NaHCO_3$, $MgCO_3$ and $CaCO_3$ when heated shows a loss of 1·19 g. The residual mixture when treated with excess of HCl gave CO_2 which was found to be 112 ml at S.T.P. Calculate the percentage composition of the mixture.
[*Ans.* $NaHCO_3$ = 31·34%, $MgCO_3$ = 31·34%, $CaCO_3$ = 37·32%]

12. A sample of a mixture of NaCl and NaBr weighing 0·1809 g is treated with $AgNO_3$ solution to give 0·3715 g of precipitate. Calculate the content of NaCl and NaBr in the mixture. [Na = 23, Cl = 35·5, Br = 79·9, Ag = 107·87] [*Ans.* NaCl = 0·06613 g, NaBr = 0·11477 g] [*WBJEE '92*]

13. One gram of a mixture of $NaCO_3$ and $NaHCO_3$ was treated with excess of dil. HCl. The volume of CO_2 evolved was found to be 240 cc at 27°C and 778·5 mm pressure. Calculate the percentage composition of the mixture. Aq tension at 27°C is 18·5 mm. [*Ans.* Na_2CO_3 = 87·2%, $NaHCO_3$ = 12·8%]

14. Calculate (i) the weight of MnO_2 and (ii) the volume of HCl of specific gravity 1·12 and containing 40% HCl by weight, needed to produce 1·78 litres of Cl_2 at S.T.P. [Mn = 54·9, Cl= 35·5]
[*Ans.* MnO_2 = 6·905 g, vol of HCl = 25·9 ml] [*I.I.T. '77*]

15. 4·5 g of $MgCO_3$ were added to double its weight of dil. H_2SO_4. After the completion of the reaction it was found that 0·3 g of $MgCO_3$ remained unreacted. Calculate the percentage strength of H_2SO_4 and volume of CO_2 formed at 27°C and 760 mm pressure.
[*Ans.* H_2SO_4 = 54·44%, CO_2 = 1230·7 ml]

16. A mixture of Al and Zn weighing 1·67 g was completely dissolved in acid and the evolved 1·69 litres of hydrogen was measured at 273 K and one atoms. pressure. What was the weight of Al in the original mixture ? [*Ans.* Al = 1·229 g] [*MLNR '91*]

17. When 3·2 g of sulphur is vapourised at 450°C and 723 mm pressure, the vapour occupies a volume of 780 ml. What is the molecular formula of sulphur vapour under these conditions ? [*Ans.* S_8] [*I.I.T. '68*]

18. Striking wooden match involves the combustion of P_4S_3 to produce a white smoke of P_4O_{10} and gaseous sulphur dioxide. Calculate the volume of SO_2 that is formed at 27°C and 770 mm of Hg from the combustion of 0·0546 g of P_4S_3 [P = 31, S = 32, O = 16]. [*Ans.* 18·1 ml] [*W.B.J.E.E. '93*]

19. Brass is an alloy of copper and Zinc. A sample of brass weighing 5·793 g when treated with excess of dil. H_2SO_4 gave 324 ml of dry hydrogen at 20°C and 750 mm pressure. What is the percentage by weight of copper in the alloy ? [*Ans.* 85·025%] [*I.I.T. '68*]

20. A flash bulb used for taking photograph contains 30 ml of O_2 at 27°C and 780 mm pressure. Supposing that the metal wire flashed is pure Al which is oxidised to Al_2O_3 in the process of flashing, calculate the minimum weight of Al wire that is to be used for maximum efficiency [O = 16, Al = 27].
[*Ans.* 0·045 g] [*I.I.T. '68*]

21. Calculate the volume of air containing 21% by volume of O_2 at NTP required to convert 294 ml of SO_2 to SO_3 under the same conditions. [*Ans.* 700 ml.]

22. 13 g of a mixture of $KClO_3$ and KCl on heating evolves O_2, which reacts completely with 7·484 litre of hydrogen at 27°C and 750 mm pressure. Find the percentage composition of $KClO_3$ and KCl in the mixture. [*Ans.* 94·24% ; 5·76%]

23. How many gram of pure $CaCO_3$ will be required to produce 1 litre of CO_2 at 27°C and 760 mm pressure ? If a particular hydrochloric acid soln. containing 22% of acid by weight, then how much quantity of this acid will be required to produce 1 litre of CO_2 at 27°C and 760 mm pressure from pure $CaCO_3$? [*Ans.* 4·06 g, 13·45g] [*W.B.H.S. '90*]

24. One litre of an acidified solution of $KMnO_4$ containg 15·8 g of $KMnO_4$ is decolourised by passing sufficient amount of SO_2. If the SO_2 is produced by roasting of iron pyrites (FeS_2) what will be the amount of pyrites required to produce the necessary amount of SO_2 ? [*Ans.* 15 g] [*I.I.T. '74*]

25. 10 ml of a gaseous hydrocarbon was burnt completely in 80 ml of O_2 at N.T.P. The remaining gas occupied 70 ml at N.T.P. This volume became 50 ml on treatment with KOH solution. What is the emperical formula of the hydrocarbon ? [*Ans.* C_2H_4] [*I.I.T. '76*]

26. 20 ml of a gaseous hydrocarbon were exploded with 100 ml of O_2. On cooling to room temperature the volume of the gas mixture was 70 ml. Introduction of KOH reduced the volume to 10 ml, the residual gas being O_2. Calculate the molecular formula of the hydrocarbon. [*Ans.* C_3H_6]

27. 5·2 ml of a gaseous hydrocarbon were exploded with excess of O_2 and the products cooled. A contraction of 7·8 ml was observed. A further contraction of 10 ml was noted on treatment with aqueous potash. Find out the molecular formula of the hydrocarbon. [*Ans.* C_2H_2]

28. 15 ml of a gaseous hydrocarbon required for complete combustion 357 ml of air (21% of O_2 by volume) and the gaseous products occupied 327 ml. (all volumes being measured at N.T.P.). What is the formula of hydrocarbon ? [*Ans.* C_3H_8]

29. A gaseous hydrocarbon was exploded with excess of O_2. On cooling to room temperature a contraction of 1·5 times the volume of hydrocarbon taken was observed. A further contraction equal to double the volume of hydrocarbon was noted on treatment with aqueous potash. What is the molecular formula of the hydrocarbon ? [*Ans.* C_2H_2]

30. 100 ml of a mixture of CO, CH_4 and H_2 are mixed with 300 ml of O_2 and fired. After cooling, the resulting gas occupied 285 ml and after absorption by potash 205 ml of O_2 remained. Find the composition of the mixture. [*Ans.* CO = 50 ml, CH_4 = 30 ml, H_2 = 20 ml]

31. 10 ml of a mixture of CH_4, CO and N_2 was exploded with 20 ml of O_2. The gaseous products when cooled occupied 20 ml, of which 8 ml were absorbed by potash and further 10 ml by alkaline pyrogallol. Calculate the composition of the mixture. [*Ans.* CH_4 = 4 ml, CO = 4 ml, N_2 = 2 ml]

32. A gaseous hydrocarbon requires 5 times its volume of O_2 for its complete combustion. The gaseous products on cooling and subsequent treatment with caustic Potash, a contraction equal to three times the volume of the original hydrocarbon is observed. Find out the molecular formula of the hydrocarbon. [*Ans.* C_3H_8]

33. 10 ml of a mixture of CH_4, CO and N_2 when exploded with excess of O_2 gave a contraction of 6·5 ml. There was a further contraction of 7 ml when the residual gas was treated with KOH. What was the composition of the original mixture ? [*Ans.* CH_4 = 2 ml, CO = 5 ml, N_2 = 3 ml]

34. 50 ml of water gas which contains CO_2 are exploded with 50 ml of O_2. The volume after the explosion becomes 50 ml. On treatment with KOH solution the volume is further reduced to 26·25 ml. Find the percentage composition of the mixture. [*Ans.* CO = 42·5%, H_2 = 52·5%, CO_2 = 5%]

35. 20 ml of a gaseous hydro carbon were exploded with O_2 avoiding excess. After cooling the volume contracts by 60 ml. The vapour density of the hydrocarbon is 22. Find out the formula of the hydrocarbon.

[*Ans.* C_3H_8]

36. 30 ml of a mixture of CH_4 and H_2 were mixed with 60 ml of O_2 and the mixture was exploded. On cooling the mixture was found to be 52·5 ml. On treatment with aqueous KOH the volume was reduced to 37·5 ml. Find the weight of each of the gases in the mixture. (All volumes were measured at N.T.P.).

[*Ans.* CH_4 = 0·0108 g, H_2 = 0·00135 g]

37. 25 ml of O_2 were subjected to silent electric discharge. The volume of the ozonised oxygen was found to be 20 ml. Find the composition of the ozonised oxygen. [*Ans.* O_2 = 10 ml, O_3 = 10 ml]

38. 0·0265 g of a liquid hydrocarbon is mixed with excess of O_2 and exploded in an eudiometer. On cooling a contraction of 21 ml is observed (volumes measured at N.T.P.). The vapour density of the hydrocarbon is 42. Find out its molecular formula. [*Ans.* C_6H_{12}]

39. 30 ml of a mixture of CO and CO_2 were mixed with 10 ml of O_2 and exploded in an eudiometer. The residual gas on treatment with aqueous KOH 5 ml of O_2 were left. Find out the composition of the mixture (volumes were measured at the same temperature and pressure).

[*Ans.* CO = 10 ml, CO_2 = 20 ml] [*W.B.J.E.E. '83*]

40. 500 ml of a hydrocarbon gas when burnt in excess of O_2 yields 2500 ml of carbon dioxide and 3 litres of water vapour. What is the formula of the hydrocarbon ? All volumes are measured of the same temperature and pressure. [*Ans.* C_5H_{12}] [*I.I.T. '74*]

41. A hydrated sulphate of a metal contained 8·1% metal and 43·2% of sulphate by weight. Assuming that the specific heat of the metal to be 0·242, determine the formula of the hydrated sulphate.
[**Ans.** $M_2(SO_4)_3$, 18 H_2O] [*I.I.T. '77*]

42. An organic compound containing carbon, hydrogen and oxygen contains 64·9% of carbon, 13·5% of H_2. When vaporised in Victor Meyer apparatus, 0·185 g of it displaced 56 ml of air at S.T.P. Write down the structure of the compound. [**Ans.** $C_4H_{10}O$] [*W.B.J.E.E. '92*]

43. 0·05 g of a liquid hydrocarbon was burnt completely in excess of dry oxygen. The contraction observed on cooling the residual gas mixture after combustion was 40 ml. In a Victor Meyer apparatus 0·2 g of the vapour of the same hydrocarbon displaces 53·3 ml. of dry air at N.T.P. Calculate the molecular formula of the hydrocarbon. [**Ans.** C_6H_{12}] [*W.B.J.E.E. '90*]

44. 1·279 g of an organic compound containing C, H, O and N gave 1·6 g of CO_2 and 0·77 g of water on combustion. Analytical result shows that 0·8125 g of the compound contains 0·108 g of N_2. Calculate the emperical formula of the compound. [**Ans.** $C_3H_7NO_3$]

45. An organic compound contains 40·65% carbon, 8·55% hydrogen and 23·7% nitrogen. Vapour density of the compound is 23·5. Find out the emperical formula and molecular formula of the compound.
[**Ans.** C_2H_5NO]

46. A gaseous hydrocarbon contain 85·62% of carbon. The density of the hydrocarbon is found to be 1·26 g/litre. Calculate its molecular formula. [**Ans.** C_2H_4]

47. An organic monobasic acid gave the following percentage composition : C = 70·59, H = 5·88, O = 23·53. 0·272 g of the acid required 20 ml of N/10 NaOH for complete neutralisation. Deduce the emperical formula and molecular formula of the acid. [**Ans.** C_4H_4O, mol. $C_8H_8O_2$]

48. An organic liquid contains 12·8% carbon, 2·1% hydrogen and 85·1% bromine. 0·188 g of it in Victor Meyer apparatus displaced 24·2 ml of moist air measured at 14°C and 752 mm pressure. Find the molecular formula of the substance (Aqueous tension at 14°C = 12 mm) [**Ans.** $C_2H_4Br_2$]

49. An organic dibasic acid contains C = 17·39%, H = 1·45% and Br = 57·97%. The vapour density of its ethyl ester is 166. Determine the molecular formula of the acid. [**Ans.** $C_4H_4Br_2O_4$]

50. 0·0833 mole of a carbohydrate contains 1 g of hydrogen. What is the molecular formula of the carbohydrate ? [**Ans.** $C_6H_{12}O_6$]

51. 1 g of a metal (At wt 56) produces 4·9642 g of hydrated sulphate. 1 g of this hydrated sulphate on being heated liberates 0·4532 g of water. What is the simplest formula of the hydrated sulphate ? (*W.B.J.E. '91*)

Ans. 1 g of hydrated sulphate contains 0·4532 g of H_2O.
4·9642 g of hydrated sulphate contains 0·4532 × 4·9642 = 2·249 g of H_2O
$\therefore$ The amount of (SO_4 + H_2O) in 4·9642 g of hydrated sulphate = 4·9642 − 1 = 3·9642 g.
Amount of sulphate = 3·9642 − 2·249 = 1·715

	Ratio of atoms or radicals	Simplest ratio of atoms or molecule or radicals
Metal M	$\frac{1}{50} = 0{\cdot}0178$	$\frac{0{\cdot}0178}{0{\cdot}0178} = 1$
SO_4	$\frac{1{\cdot}715}{96} = 0{\cdot}0178$	$\frac{0{\cdot}0178}{0{\cdot}0178} = 1$
H_2O	$\frac{2{\cdot}249}{18} = 0{\cdot}1249$	$\frac{0{\cdot}1249}{0{\cdot}0178} = 7$

$\therefore$ The simplest formula of hydrated sulphate is MSO_4, $7H_2O$.

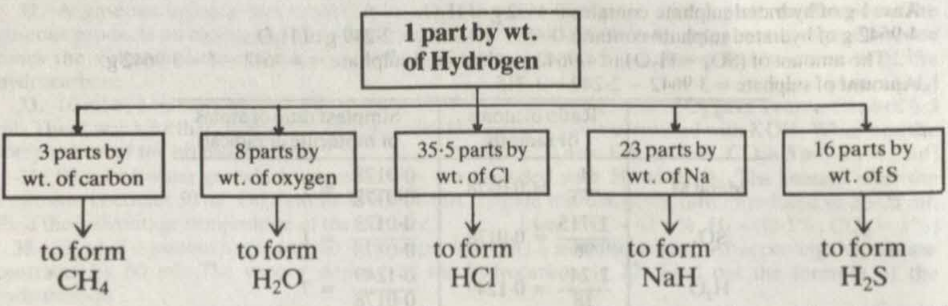
EQUIVALENT WEIGHT AND ATOMIC WEIGHT

4

4.1. Introduction.

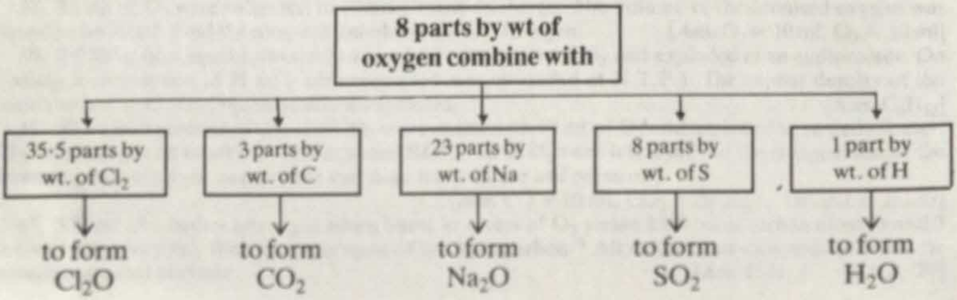
The law of constant proportions states that *whenever an element combines with another element to form a pure chemical compound, it does so in a definite or fixed ratio by weight.* Again it follows from the law of reciprocal proportions that *every element must have a fixed weight in which, or in simple multiple of which, it combines with other elements.* Thus every element has a combining weight or more specifically an equivalent weight, which gives the relative proportions in which it combines with the other elements. The numerical values of the combining or equivalent weight control the way in which elements combine to form chemical compounds.

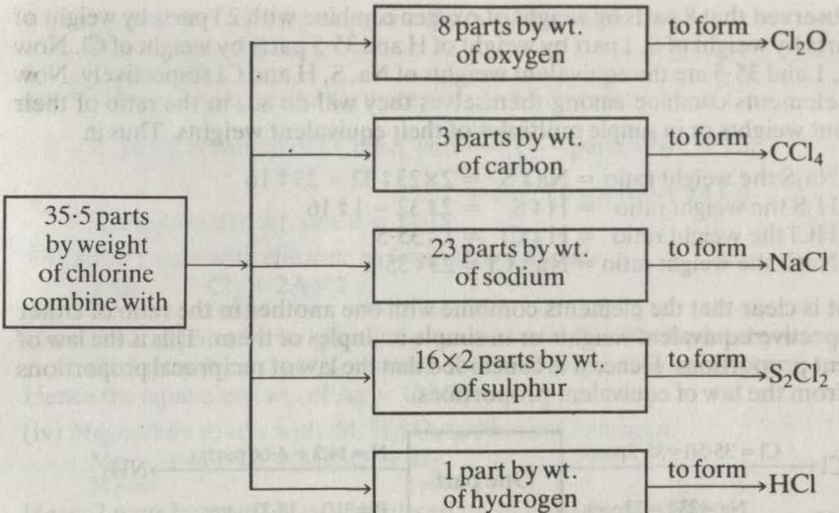
In order to determine the combining or equivalent weight of an element, it is necessary to select a fixed weight of some element (s) as standard. It has been observed that *8 parts by weight of oxygen always combines with 1·008 parts by weight of hydrogen or 3 parts by weight of carbon or 16 parts by weight of sulphur or 23 parts by weight of sodium or 35·5 parts by weight of chlorine.* Therefore, whenever these elements combine among themselves, e.g., carbon with chlorine to form CCl_4, or sodium with sulphur to form Na_2S etc., the elements will combine in the ratio of the above numbers or in simple multiples of these numbers.



The combining weight ratio of carbon, oxygen, chlorine, sodium and sulphur, if they combine among themselves will be 3 : 8 : 35·5 : 23 : 16 or simple multiples of them.

Instead of hydrogen if we take oxygen or chlorine as the standard, the following charts exhibit the reacting capacity of different elements.




35·5 parts by weight of chlorine combine with
8 parts by wt. of oxygen
to form
Cl_2O
3 parts by wt. of carbon
to form
CCl_4
23 parts by wt. of sodium
to form
NaCl
16×2 parts by wt. of sulphur
to form
S_2Cl_2
1 part by wt. of hydrogen
to form
HCl

The above three charts clearly reveal that the elements combine with a fixed weight of hydrogen, oxygen or chlorine. Therefore it can be argued that whenever the elements combine among themselves they must do so either in the ratio of those weights or in some multiples or submultiples of those weights. As for examples—

(i) Carbon combines with O_2 to form CO_2
$C + O_2 = CO_2$. $\qquad C : O = 3 : 8$
(ii) Carbon reacts with chlorine to form CCl_4
$C + 2Cl_2 = CCl_4$ $\qquad C : Cl = 12 : 4\times35{\cdot}5 = 3 : 35{\cdot}5$
(iii) Sodium reacts with chlorine to form sodium chloride.
$2Na + Cl_2 = 2NaCl$ $\qquad Na : Cl = 2\times23 : 2\times35{\cdot}5 = 23 : 35{\cdot}5$
(iv) Carbon forms carbon disulphide by reacting with sulphur.
$C + 2S = CS_2$ $\qquad C : S = 12 : 2\times32 = 3 : 16$

Thus the weight ratio of

$$C : O : Cl : Na : S = 3 : 8 : 35{\cdot}5 : 23 : 16$$

These numbers of weights are known as the *equivalent weight of the respective elements.*

• The law of reciprocal proportions is a corollary of the law of equivalent proportions.

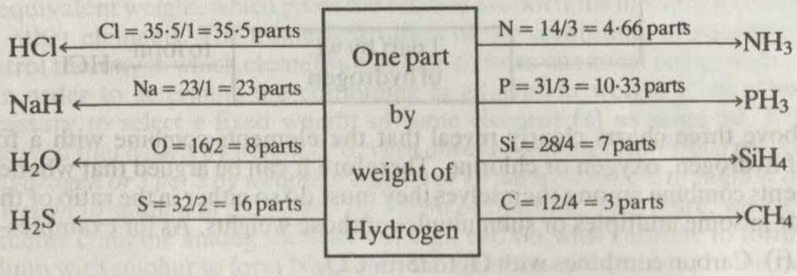
The idea that each element has a combining weight or equivalent weight of its own, follow directly as a corrolary from the law of reciprocal proportions. As for example, the ratio of the weights of the elements present in Na_2O, SO_2, H_2O and Cl_2O is shown in the following table.

Compound	Weight ratio of the elements	Wt. of other elements that combine with a fixed wt. of O_2
Na_2O	$O : Na = 16 : 2\times23$	$8 : 23$
SO_2	$O : S = 32 : 32$	$2\times8 : 16$
H_2O	$O : H = 16 : 2$	$8 : 1$
Cl_2O	$O : Cl = 16 : 2\times35{\cdot}5$	$8 : 35{\cdot}5$

It is observed that 8 parts by weight of oxygen combine with 23 parts by weight of Na, 8 parts by weight of S, 1 part by weight of H and 35·5 parts by weight of Cl. Now 23, 8×2, 1 and 35·5 are the equivalent weights of Na, S, H and Cl respectively. Now if these elements combine among themselves they will do so, in the ratio of their equivalent weights or in simple multiples of their equivalent weights. Thus in

Na_2S the weight ratio $= Na : S = 2\times23 : 32 = 23 : 16$
H_2S the weight ratio $= H : S = 2 : 32 = 1 : 16$
HCl the weight ratio $= H : Cl = 1 : 35{\cdot}5$
NaCl the weight ratio $= Na : Cl = 23 : 35{\cdot}5$

Thus it is clear that the elements combine with one another in the ratio of either their respective equivalent weights or in simple multiples of them. This is the law of equivalent proportions. Hence it is concluded that the law of reciprocal proportions follows from the law of equivalent proportions.



4.2. Equivalent weight of an element.

The equivalent weight of an element is the number of parts by weight of the element which combine with or replace from a chemical combination, 8 parts by weight of oxygen, or 1·008 parts by weight of hydrogen or 35·46 parts by weight of chlorine.

$$\text{Thus, Equivalent wt. of an element} = \frac{\text{wt. of the element} \times 8}{\text{wt. of the combined or replaced } O_2}$$

$$\text{or, Equivalent wt. of an element} = \frac{\text{wt. of the element} \times 1{\cdot}008}{\text{wt. of the combined or replaced } H_2}$$

$$\text{or, Equivalent wt. of an element} = \frac{\text{wt. of the element} \times 35{\cdot}5}{\text{wt. of the combined or replaced } Cl_2}$$

Since equivalent weight of an element represents ratio of weights, *it has no unit—it is a pure number.*

Consdering the volume ratio instead of weight ratio, *the equivalent weight of an element may be defined as the number of parts by weight of the element which combine with or replace from a compound 11200 ml of hydrogen or 5600 ml of oxygen or 11200 ml of chlorine at N.T.P.*

Examples :

(i) *Sodium* combines with hydrogen to form *sodium hydride.*

$$\underset{2\times23}{2Na} + \underset{2}{H} = 2NaH$$

Here, 2 parts by weight of H_2 combine with 2×23 parts by wt. of Na
∴ 1 part by weight of H_2 combines with 23 parts by wt. of Na
∴ The equivalent wt. of Na = 23.

(ii) *Oxygen* reacts with hot copper to form *cupric oxide.*

$$\underset{2\times63\cdot5}{2Cu} + \underset{32}{O_2} = 2CuO$$

Here, 32 parts by weight of O_2 react with $2\times63\cdot5$ parts by wt. of Cu.

$$\therefore\ 8 \text{ parts by weight of } O_2 \text{ react with } \frac{2\times63\times8}{32} \text{ parts by wt. of Cu.}$$
$$= 31\cdot75 \text{ parts by wt. of Cu}$$

$\therefore$ The equivalent wt. of Cu = $31\cdot75$

(iii) *Silver* reacts with chlorine to form *silver chloride.*

$$\underset{2\times107\cdot98}{2Ag} + \underset{2\times35\cdot5}{Cl_2} = 2AgCl$$

Here, $2\times35\cdot5$ parts by weight of Cl_2 combine with $2\times107\cdot98$ parts by wt. of Ag

$\therefore$ $35\cdot5$ parts by wt. of Cl_2 combine with $107\cdot98$ parts by wt. of Ag.

Hence the equivalent wt. of Ag = $107\cdot98$

(iv) *Magnesium* reacts with dil. H_2SO_4 to liberate *hydrogen.*

$$\underset{24\text{ parts}}{Mg} + H_2SO_4 = MgSO_4 + \underset{2\text{ parts.}}{H_2}$$

Here, 2 parts by wt. of H_2 are displaced by 24 parts by wt. of Mg

$$\therefore\ 1 \text{ part by wt. of } H_2 \text{ is displaced by } \frac{24\times1}{2} = 12 \text{ parts by wt. of Mg}$$

Hence the equivalent wt. of Mg = 12.

• **Gram equivalent weight :** Equivalent weight is a pure number—it has no unit. It is however useful to express this quantity in gram and thereby use it to denote a definite amount of material.

The gram equivalent weight of an element is its equivalent weight expressed in gram i.e., *gram equivalent weight or gram equivalent of an element is defined as the weight of an element in gram that combines with or replaces from a compound 1·008 g of hydrogen or 8 g of oxygen or 35·5 g of chlorine.*

Thus *equivalent wt. of magnesium* = 12.
$\therefore$ 12 g of magnesium = 1 gram equivalent of Mg.
Similarly *equivalent wt. of sodium* = 23
$\therefore$ 23 g of Na = 1 gram equivalent of Na.
$11\cdot5$ g of Na = $0\cdot5$ gram equivalent of Na.
92 g of Na = 4 gram equivalents of Na.

• Equivalent weight of radicals.

Equivalent weight of a radical is a number showing how many parts by weight of the radical can combine with 1·008 parts by weight of hydrogen, or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine.

Examples :

(i) Thus in HNO_3, 1 part by weight of hydrogen combines with 62 parts by weight of NO_3^- radical.

$\therefore$ The eq. wt. of NO_3^- radical = 62.

(ii) In NH_4Cl, $35\cdot5$ parts by weight of chlorine combine with 18 parts by weight of NH_4^+ radical.

$\therefore$ The eq. wt. of NH_4^+ = 18.

(iii) In H_2SO_4, 2 parts by weight of hydrogen combine with 96 parts by weight of SO_4^{--}.

Hence the eq. wt. of SO_4^{--} = 96/2 = 48.

- **Equivalent weight of a salt.**

The equivalent weight of a salt is number showing how many parts by weight of the salt contain or react with 8 parts by weight of active oxygen or 1·008 parts by weight of hydrogen or an equivalent of any other active element.

Thus 106 g of Na_2CO_3 contain 46 g of Na.

The hydrogen equivalent of Na present in the molecule = 46/23 = 2.

$\therefore$ Equivalent wt. of Na_2CO_3 = 106/2 = 53.

Alternatively, the equivalent weight of a salt refers to that weight of the salt that contains 1 equivalent weight of the cation.

$$\text{Eq. wt. of a salt} = \frac{\text{Molecular wt. or formula wt. of the salt}}{\text{Number of cations} \times \text{valency of cation}}$$

$$\text{Thus, the eq. wt. of } Na_2CO_3 = \frac{106}{2\times 1} = 53$$

$$\text{The eq. wt. of } Al_2(SO_4)_3 = \frac{342}{2\times 3} = 57.$$

Again the equivalent wt. of a salt is the sum of the equivalent weights of the elements or radical present in it.

Thus, equivalent wt. of $Al_2(SO_4)_3$ = eq. wt. of Al + eq. wt. of SO_4^{--} = 9 + 48 = 57

Detailed discussion on equivalent weights of acids and bases are discussed in acidimetry and alkalimetry chapter.

Eq. wt. of some salts are shown below :

Salts	Eq. wt. of elemets or radicals	Eq. wt. of salt
$MgSO_4$	Mg = 12 ; SO_4^{--} = 48	12 + 48 = 60
$CaCO_3$	Ca = 20 ; CO_3^{--} = 30	20 + 30 = 50
$KClO_3$	K = 39 ; ClO_3^- = 83·5	39 + 83·5 = 122·5
NH_4Cl	NH_4^+ = 18 ; Cl^- = 35·5	18 + 35·5 = 53·5
AgCl	Ag = 107·88 ; Cl^- = 35·5	107·88 + 35·5 = 143·38

- **Relation between equivalent weight & atomic weight.**

Let the equivalent weight of an element be *E*, its atomic weight be *A* and its velency be *V*.

It is known to us that valency of an element is measured by the number of hydrogen atoms which combine with 1 atom of the element.

$\therefore$ *V* atoms of hydrogen combine with 1 atom of the element

i.e., $V \times 1{\cdot}008$ parts by weight of hydrogen combine with *A* parts by weight of the element.

$$\therefore\ 1{\cdot}008 \text{ parts by weight of hydrogen combine with } \frac{A\times 1{\cdot}008}{V\times 1{\cdot}008}$$

$$= \frac{A}{V} \text{ parts by wt. of element}$$

By definition the above ratio is equivalent wt. of the element (*E*)

or, $E = \dfrac{A}{V}$ or, $A = E \times V$

or, **Atomic wt. of an element = Eq. wt. × valency.**

The above relation can also be deduced on the basis of the equivalent weight of oxygen.

Let the symbol of the element = M, Valency = V, Eq. wt. = E, At. wt. = A. Since valency of the element is V and valency of oxygen is 2, the formula of the oxide = M_2O_V

Now,

$16 \times V$ parts by wt. of oxygen combine with $A \times 2$ parts by wt. of M

$$8 \text{ parts by wt. of oxygen combine with } \frac{A\times2\times8}{16\times V} \text{ parts by wt. of } M$$

$$= \frac{A}{V} \text{ parts by wt. of } M.$$

By definition $\frac{A}{V}$ represents eq. wt. of the element, hence $E = \frac{A}{V}$

or, **Eq. wt. of an element** $= \dfrac{\textbf{At. wt.}}{\textbf{Valency}}$

- **Equivalent wt. is not constant.**

On the basis of the relation Eq. wt. $= \dfrac{\text{Atomic wt.}}{\text{Valency}}$ it can be logically concluded that since the atomic weight of an element is constant according to Dalton, the equivalent weight of an element is inversely proportional to its valency i.e., $E \propto \frac{1}{V}$. Consequently the equivalent weight of an element will change with the change of its valency. Now if the concerned element has constant valency, then and then only its equivalent weight will be constant.

But the *transitional elements* or *'d' block elements* are characterised by variable valencies. So these elements will have variable equivalent weights. Thus—

(1) (i) The valency of copper in cuprous oxide is 1.

$\therefore$ The equivalent wt. of Cu(*ous*) where it is monovalent $= \dfrac{63\cdot5}{1} = 63\cdot5$

(ii) The valency of copper in cupric oxide is 2.

$\therefore$ The equivalent wt. of Cu(*ic*) where it is bivalent $= \dfrac{63\cdot5}{2} = 31\cdot75$

In Cu_2O, 8 parts by weight of oxygen combine with 63·5 parts by weight of Cu ; while in CuO, 8 parts by weight of oxygen unite with 31·75 parts by weight of copper.

(2) The atomic weight of iron is 55·85. The valencies of iron in *'ous'* and *'ic'* compounds are 2 and 3 respectively. So the eq. wt. of Fe(*ous*) $= \dfrac{55\cdot85}{2} = 27\cdot925$

and the eq. wt. of Fe(*ic*) $= \dfrac{55\cdot85}{3} = 18\cdot616$

'The equivalent wt. of an element depends on the reaction it undergoes'—this statement can be explained with the help of the following pair of reactions—

(i) $Fe + 2HCl = FeCl_2 + H_2$

(ii) $2Fe + 3Cl_2 = 2FeCl_3$

In the first reaction 55·85 parts by weight of Fe liberate 2·016 parts by weight of hydrogen from hydrochloric acid.

$$\therefore \text{ Eq. weight of Fe} = \frac{55\cdot85\times1\cdot008}{2\cdot016} = \frac{55\cdot85}{2} = 27\cdot925$$

$$\text{or, the Eq. wt. of Fe} = \frac{\text{Atomic wt.}}{\text{Valency}} = \frac{55\cdot85}{2} = 27\cdot925$$

In the second reaction $\frac{55 \cdot 85}{3}$ or 18·616 parts by weight of iron combine with 35·46 parts by weight of chlorine to form $FeCl_3$. So the equivalent weight of Fe(*ic*) is 18·616.

i.e., the eq. wt. of Fe(*ic*) $= \frac{55 \cdot 85}{\text{Valency}} = \frac{55 \cdot 85}{3} = 18 \cdot 616$

Therefore, it may be concluded that although the eq. wt. of an element is a fundamental quantity, its value depends upon the type of reaction it undergoes.

- **Eq. wt. of an element changes with the change of oxidation number.**

$$4\overset{+2}{Fe}O + O_2 = 2\overset{+3}{Fe_2}O_3$$

In FeO, since the O.N. of Fe is +2, its eq. wt. will be $\frac{55 \cdot 85}{2} = 27 \cdot 925$

and in Fe_2O_3, since the O.N. of Fe is +3, its eq. wt. $= \frac{55 \cdot 85}{3} = 18 \cdot 616$

The relation between the equivalent weight and the atomic weight of an element indicates that when the valency of an element is 1, then its atomic weight will be the same as its equivalent weight. Thus, *the atomic weights of monovalent elements like Na, K, Ag, F, Cl, Br etc., are the same as their equivalent weights.*

e.g., valency of sodium = 1,   atomic weight of Na = 23

$\therefore$ The equivalent weight of Na $= \frac{\text{Atomic wt.}}{\text{Valency}} = \frac{23}{1} = 23.$

4.3. Electronic approach.

All ionic reactions can be interpreted in terms of loss or gain of electron(s).

Equivalent weight of an element, an oxidising agent or a reducing agent is the ratio of the atomic weight of the element or the molecular weight of the compound to the number of electron(s) lost or gained during the particular reaction.

$$\text{Eq. wt.} = \frac{\text{Molecular wt. or Atomic wt.}}{\text{Number of electron lost or gained per molecule or atom}}$$

(1) In the following reaction

$$2Fe + 3Cl_3 = 2FeCl_3$$

As 3 electrons are lost by 1 atom of Fe, $Fe - 3e \rightleftharpoons Fe^{+++}$

Eq. wt. of Fe $= \frac{\text{At. wt.}}{3} = \frac{55 \cdot 85}{3} = 18 \cdot 616$

(2) Again in $2FeCl_2 + Cl_2 = 2FeCl_3$

$$Fe^{++} - e \rightleftharpoons Fe^{+++}$$

Eq. wt. of $FeCl_2 = \frac{\text{Mol. wt. of } FeCl_2}{1}$

When $FeCl_2$ is reduced to metallic Fe,

$$Fe^{++} + 2e \rightleftharpoons \overset{0}{Fe}$$

Eq. wt. of $FeCl_2 = \frac{\text{Mol. wt. of } FeCl_2}{2}$

(3) **Eq. wt. of $KMnO_4$ is different in different media.**

(a) ***In strong acid medium :***

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$$

Eq. wt. of $KMnO_4 = \frac{\text{Mol. wt. of } KMnO_4}{5} = \frac{158}{5} = 31 \cdot 6$

(b) *In weakly acidic medium :*

$$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$$

$$\text{Eq. wt. of } KMnO_4 = \frac{158}{3} = 52{\cdot}66$$

(c) *In strongly alkaline medium :*

$$MnO_4^- - e \rightleftharpoons \underset{\text{(Manganate ion)}}{MnO_4^{--}}$$

$$\text{Eq. wt. of } KMnO_4 = \frac{158}{1} = 158$$

(d) *In weakly alkaline medium :*

$$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$$

$$\text{Eq. wt. of } KMnO_4 = \frac{158}{3} = 52{\cdot}66$$

Hence it can be concluded that Eq. wt. of an element or compound depends upon the *nature, medium* and *type* of reaction.

4.4. Different methods of the determination of equivalent weights of elements.

[A] Determination of equivalent weights of metals.

Principles : (i) Metals which are above hydrogen in the electro chemical series, can displace hydrogen from dilute acids or alkalis e.g., **Zn, Al, Mg, Fe,** etc., liberate hydrogen quantatively by reacting with dil. H_2SO_4 or HCl. The volume of hydrogen liberated by a known weight of metal is converted to the volume at N.T.P. Its weight is calculated by multiplying the volume at N.T.P. with 0·000089. The equivalent weight of the metal is the weight that liberates 1·008 g of hydrogen.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Mg
Al
Zn
Fe
Sn
Pb
H

(ii) Metals which are below hydrogen in the electrochemical series e.g., **Cu, Hg, Ag** etc. cannot liberate hydrogen from dilute acids or alkalis, but they combine with oxygen to form their oxides. In finding out the equivalent weight of such metal, a known weight of the metal is dissolved in conc. HNO_3, and the resulting solution is slowly evaporated to dryness to form the corresponding nitrate. The nitrate thus obtained is then strongly heated to form the oxide of the metal whose constant weight is taken.

H
Cu
Hg
Ag

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

The difference between the weights of the oxide formed and that of the metal taken gives the weight of the oxygen which has combined with the metal. Thus according to definition,

$$\text{Eq. wt. of the metal} = \frac{\text{wt. of the metal taken} \times 8}{\text{wt. of oxygen combined}}$$

(iii) Noble metals like **Au, Pt** etc., occur well below hydrogen in the electrochemical series. Hence they neither liberate H_2 from acid nor do they react with O_2. The metals are brought into solution either by reacting with *aqua regia* or are converted into chloride by other methods. The weight of chlorine is found by subtracting the weight of the metal from

Ag
Au
Pt

that of its chloride. The equivalent weight of the metal is the weight that combines with 35·5 parts by weight of chlorine.

(1) Hydrogen displacement method :

The method is applicable for those metals which occur above hydrogen in the electrochemical series except the alkali metals since the later react with acids violently sometimes with explosion.

A. **Displacement of hydrogen from acid :**

[A] **Principle :**

A known weight of the metal (Mg, Zn, Fe, Al etc.) is allowed to react with excess of dilute H_2SO_4 or HCl and the liberated hydrogen is collected in a graduated tube by the displacement of water. The volume of hydrogen thus obtained is converted to the volume at N.T.P. Its weight is calculated by multiplying the volume at N.T.P. with 0·000089 (Avogadro's law). The equivalent weight of the metal is the weight that liberates 1·008 g of hydrogen.

$$\text{i.e., Equivalent weight of the metal} = \frac{\text{wt. of the metal} \times 1{\cdot}008}{\text{wt. of liberated } H_2}$$

[B] **Procedure :**

(i) A definite weight (about 0·1 g) of a piece of pure zinc is taken and is placed at the bottom of a beaker. The piece of zinc is then covered with an inverted funnel, Water is added in the beaker so that the whole of the stem of the funnel remains under water.

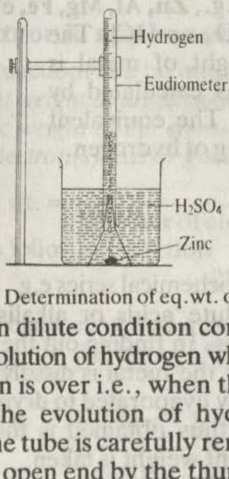


Fig 4.1 : Determination of eq.wt. of Zinc

(ii) An eudiometer tube filled completely with water is inverted over the stem of the funnel so that the whole of the stem of the funnel remains inside the tube. The eudiometer is then clamped to a stand. Since H_2SO_4 does not react with pure zinc, a few drops of $CuSO_4$ solution is added into the water of the beaker.

(iii) Moderately strong H_2SO_4 is next added to the water in the beaker. As soon as H_2SO_4 in dilute condition comes in contact with the piece of zinc, reaction starts with the evolution of hydrogen which is collected inside the eudiometer tube. (iv) When the reaction is over i.e., when the piece of zinc is completely dissolved in sulphuric acid and the evolution of hydrogen is stopped, the tube is carefully removed by closing the open end by the thumb and is placed in a tall jar filled with water. The surface of water inside and outside of the tube is brought to the same level by holding the tube with a piece of paper and not with the fingers.

(v) The volume of hydrogen is noted carefully. The temperature of the room is noted with a thermometer and the atmospheric pressure with a barometer.

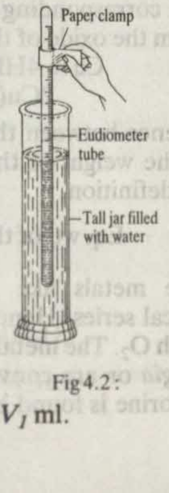


Fig 4.2 :

[C] **Calculation :**

Let the wt. of the zinc taken = *w* g.

Vol of the hydrogen at room temp. and pressure = V_1 ml.

Temp. of the room i.e., temp. of the hydrogen gas = t°C
Pressure of the atmosphere = P mm and aqueous tension at t°C = f mm
Hydrogen gas is *moist* as it is collected over water.
$\therefore$ Atmospheric pressure P = Pressure of dry hydrogen + Aqueous tension (f)
or, pressure of dry hydrogen = $(P - f)$ mm
Therefore, it may be stated that w g of Zn liberates V_1 ml. H_2 gas at t°C and $(P - f)$ mm pressure.

Let V_1 ml of hydrogen at t°C and $(P-f)$ mm pressure occupy V ml at N.T.P. Now applying Boyle's and Charle's laws we get,

$$\frac{760 \times V}{273} = \frac{(P-f) \times V_1}{273 + t}$$

$$\text{or, } V = \frac{(P-f) \times V_1 \times 273}{760 \times (273+t)} \quad \text{Let it be } x \text{ ml.}$$

From Avogadro's Law—
Weight of 22400 ml of H_2 at N.T.P. = 2 g

Weight of x ml of H_2 at N.T.P. $= \frac{2 \times x}{22400}$ g $= \frac{x}{11200}$ g

$\frac{x}{11200}$ g of hydrogen is displaced by w g of zinc

1 g of hydrogen is displaced by $\frac{w \times 11200}{x}$ g of zinc

$$\text{Eq. wt. of Zn} = \frac{w \times 11200}{x}$$

Experimentally the equivalent weight of zinc is found to be 32·84. In determining the eq. wt. of **Al** or **Sn** hydrochloric acid is used in place of dil. H_2SO_4.

B. Displacement of hydrogen from alkali.

In determining the equivalent weight of metals like **Al, Zn, Sn, Pb** etc., a known weight of the metal is allowed to react with *hot and concentrated NaOH solution* and the volume of the evolved hydrogen is noted and calculation is made as before.

(i) In the determination of equivalent wt. of zinc, a few drops of $CuSO_4$ solution are added before the starting of the hydrogen displacement—Explain why.

Pure zinc does not react with dilute H_2SO_4 or HCl appreciably. Hence a few drops of $CuSO_4$ solution are added to the acid solution. Microscopic amount of metallic zinc is consumed in displacing copper from copper sulphate solution as zinc is more electropositive element than copper.

$$Zn + CuSO_4 = ZnSO_4 + Cu\downarrow$$

The error due to the loss of zinc is so negligible that it can be within the experimental error.

But if excess of $CuSO_4$ solution is added, greater amount of metallic zinc will be used up and the error in the determination of equivalent weight will be appreciably high. Hence excess of $CuSO_4$ solution should be avoided. However in determining the equivalent of other elements by this method,it is not necessary to add $CuSO_4$ solution.

(ii) The process is not carried out in Woulfe's bottle—Explain why.

The experimental arrangement in this experiment is such that the evolved hydrogen is collected completely in the eudiometer tube by the downward displacement of water. But if zinc is kept in a woulfe's bottle and H_2SO_4 is added to it, the evolved hydrogen is mixed up with air and as a result the whole of the displaced H_2 can never be collected. Consequently Woulfe's bottle is not used in this experiment.

(iii) In the determination of equivalent wt. of zinc, the weight of zinc taken should be in between 0·08 g and 0·1 g.

If the weight of zinc taken is more than 0·1 g, the volume of the displaced hydrogen will exceed 50 ml, which is much greater than the normal capacity of the eudiometer tube. On the other hand if the weight

of zinc taken is less than 0·08 g, the volume of the displaced H_2 will be so low that the experimental errors are likely to be magnified. Hence the weight of zinc must be within a specific weight of 0·08 to 0·1 g. In case of magnesium the required weight should be very close to 0·5 g.

(iv) In the determination of equivalent weight of zinc, excess of H_2SO_4 is used— Explain why.

In order to have the complete reaction of zinc with dil. H_2SO_4 and to have the whole of the displaced hydrogen by metallic zinc taken, the acid must be in excess so that no unreacted Zn is left behind.

(v) While recording the volume of the displaced hydrogen, the eudiometer tube is held with a clamp or a piece of paper but never with fingers. This is because of the fact that the temperature of hand is sufficient to expand the gas and the result will be erroneous.

(2) Oxidation method.

The method consists in converting those metals (Cu, Hg, Ag) which cannot liberate H_2 from acids or alkalis, into their corresponding oxides by heating their nitrate salts.

• Determination of the equivalent weight of copper.

[A] Principle :

A weighed amount of metallic Cu is reacted with conc. HNO_3 and the resulting solution is evaporated to dryness. The dry nitrate thus obtained is strongly heated to get cupric oxide whose constant weight is taken.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O,$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

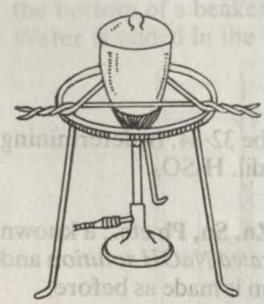


Fig 4.3 :

Now by substracting the weight of copper from that of its oxide, the weight of oxygen that combines with the known weight of Cu is obtained. Then according to the relation, eq. wt. of Cu $= \dfrac{\text{wt. of copper taken} \times 8}{\text{wt. of oxygen combined}}$

[B] Procedure :

A completely dried and clean porcelain crucible with its lid is accurately weighed. A piece of copper wire is taken in the crucible and weighed again with the lid. Conc. HNO_3 is added drop by drop to the Cu wire till it completely dissolves. Thus metallic Cu is quantitatively converted to cupric nitrate. The crucible is kept nearly covered during the reaction. It is then slowly evaporated on an asbestos board. Care must be taken to stop spirting of crystals. The green residue $[Cu(NO_3)_2]$ left in the crucible is then strongly heated till it is completely converted to black CuO. It is cooled in a desiccator and weighed. Heating and cooling of the crucible is repeated till a constant weight is obtained.

[C] Calculations :

Wt. of porcelain crucible with lid = Wg.

Wt. of crucible with lid + copper wire = W_1 g.

Wt. of copper wire = $(W_1 - W)$ g.

Wt. of crucible with lid + CuO = W_2 g.

Weight of CuO = $(W_2 - W)$ g.

Weight of oxygen that combines with Cu $= W_2 - W - W_1 + W = (W_2 - W_1)$ g.

$(W_2 - W_1)$ g of oxygen combine with $(W_1 - W)$ g of Cu

$\therefore$ 8 g of oxygen combine with $\dfrac{(W_1 - W) \times 8}{(W_2 - W_1)}$ g of Cu.

Hence equivalent weight of Cu $= \dfrac{(W_1 - W) \times 8}{(W_2 - W_1)}$

This method is also applicable for the determination of equivalent weight of Sn, Pb, Zn, Mg.

(3) Reduction method :

This method consists in the reduction of a known weight of red hot oxides of *copper, lead* by hydrogen gas to the metal which is carefully weighed in a chemical balance.

$$CuO + H_2 = Cu + H_2O$$
$$PbO + H_2 = Pb + H_2O$$

Experimental procedure :

A clean and dry porcelain boat is weighed in a chemical balance. A small amount of pure and dry metallic oxide is placed in the boat and weighed again. The boat containing the oxide is next introduced into a hard glass combustion tube clamped in horizontal position (Fig 4.4.) The boat is strongly heated by bunsen burner and pure and dry hydrogen gas is passed through one end of the boat as shown in the fig. The metallic oxide is reduced to metal under this condition of high temperature. The burner is removed, and stream of H_2 gas is continued till the residue cools to room temperature. The boat is carefully weighed. The processes of heating, cooling in H_2 and weighing are continued till the final weight becomes constant.

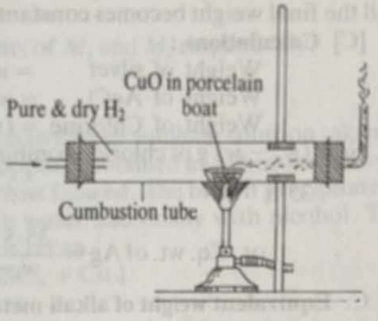


Fig 4.4 :

Calculation :

Weight of procelain boat = W g
Wt. of porcelain boat + metallic oxide = W_1 g
Wt. of metallic oxide = $(W_1 - W)$ g
Wt. of porcelain boat + metal = W_2 g
∴ Weight of metal = $(W_2 - W)$ g
Weight of oxygen = $(W_1 - W - W_2 + W)$ g
$= (W_1 - W_2)$ g

Here $(W_1 - W_2)$ g of oxygen combine with $(W_2 - W)$ g of metal

8 g of oxygen combine with $\frac{(W_2 - W) \times 8}{(W_1 - W_2)}$ g of metal

$$\text{Equivalent weight of the metal} = \frac{(W_2 - W) \times 8}{(W_1 - W_2)}$$

(4) Chloride formation method—Precipitation of the chloride :

• Determination of Equivalent weight of Silver :

[A] Principle :

Silver occurs below hydrogen in the electro-chemical series. Hence it can not liberate H_2 from acid or alkali and so hydrogen displacement method is not applicable here. Again the affinity of silver for oxygen is so poor that it can not form a stable oxide. Consequently oxidation method is not applicable here. But its chloride salt is stable. Hence silver is converted to its chloride salt from which the equivalent weight of silver is determined.

[B] **Procedure :**

A piece of pure silver is weighed and dissolved in conc. HNO_3 in a beaker, when silver nitrate is produced.

$$Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O$$

The solution is heated to ensure ready and complete dissolution of silver. It is then cooled and excess of dil. HCl is added to it when a curdy white precipitate of silver chloride is obtained. The precipitate is allowed to settle. It is then filtered through a quantitative filter paper. The precipitate of silver chloride thus obtained is washed first with dilute HNO_3 and finally with distilled water. The precipitate with the filter cone is dried in air oven. It is then ignited strongly to burn the filter paper to ash. It is cooled and weighed. The processes of heating, cooling and weighing are repeated till the final weight becomes constant.

[C] **Calculations :**

Weight of silver $= w$ g
Weight of AgCl $= w_1$ g
Weight of Chlorine $= (w_1 - w)$ g

Now $(w_1 - w)$ g of chlorine combine with w g of Ag.

$$35{\cdot}5 \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \quad \frac{35{\cdot}5 \times w}{(w_1 - w)} \text{ g of Ag.}$$

$$\text{or, Eq. wt. of Ag} = \frac{35{\cdot}5 \times w}{w_1 - w}$$

C. **Equivalent weight of alkali metals (Double decomposition method).**

The alkali metals like Na, K etc., are so active that they do not occur in nature in the free state and because of their high affinity towards air and moisture their exact weight can never be determined by chemical balance. Hence indirect method is devised to evaluate the equivalent weight of alkali metals.

A known weight of chemically pure KCl (or NaCl) is dissolved completely in distilled water taken in a beaker. A few drops of HNO_3 is added to make the solution slightly acidic. Pure silver nitrate solution is added in excess with constant stirring with a glass rod to ensure complete precipitation of chloride as curdy white precipitate of AgCl. The precipitate is allowed to settle first and then filtered through quantitative filter paper (whatman No. 41). The precipitate of AgCl is dried in air oven. The processes of heating in air oven, cooling in desiccator and weighing in a balance, are repeated till the final weight is constant.

$$KCl + AgNO_3 = AgCl \downarrow + KNO_3$$

Calculations :

Weight of KCl $= w$ g
,, ,, AgCl $= w_1$ g

$108 + 35{\cdot}5 = 143{\cdot}5$ g AgCl contain $35{\cdot}5$ g of chlorine

$$\therefore\ w_1 \quad ,, \quad ,, \quad ,, \quad \frac{35{\cdot}5 \times w_1}{143{\cdot}5} \text{ g of chlorine}$$

This amount of chlorine is present in w g of KCl.

$$\therefore \text{ The weight of potassium} = \left[w - \frac{35{\cdot}5 \times w_1}{143{\cdot}5} \right] \text{g} = x \text{ g (suppose)}$$

$\dfrac{35{\cdot}5 \times w_1}{143{\cdot}5}$ g of Cl_2 combines with x g of potassium.

$$\therefore\ 35{\cdot}5 \text{ g of } Cl_2 \text{ combines with } \frac{x \times 35{\cdot}5 \times 143{\cdot}5}{35{\cdot}5 \times w_1} = \frac{143{\cdot}5x}{w_1} \text{ g of K}$$

$\therefore$ Equivalent weight of potassium $= \dfrac{143 \cdot 5x}{w_1}$

Equivalent weight of calcium or sodium can also be determined by this method.

(5) **Displacement of one metal ion from its salt solution by another metal.**

A more eletro-positive metal can displace quantitatively a less electro-positive metal from its solution. The displacement reaction always takes place in the ratio of their equivalent weights.

Let the weight of less electro-positive metal M_1 be x g and the weight of more electro-positive metal M_2 be y g.

From Law of Equivalents, $\dfrac{x}{y} = \dfrac{E_1}{E_2}$

where E_1 and E_2 are the equivalent weights of M_1 and M_2 respectively.

Example : *Equivalent weight of copper.*

A weighed quantity of pure zinc foil is added to copper sulphate solution taken in a beaker, zinc dissolves slowly and metallic copper is obtained as a chocolate brown precipitate. It is warmed gently, cooled and then filtered. The brown precipitate of metallic copper is washed several times with water and finally with alcohol. The precipitate is dried in air oven and its weight is taken.

$$CuSO_4 + Zn = ZnSO_4 + Cu \downarrow$$

Calculation :

Weight of zinc foil = w g

Weight of copper liberated = w_1 g

According to the law of equivalent,

$$\frac{\text{Weight of copper}}{\text{Weight of zinc}} = \frac{\text{Eq. wt. of copper}}{\text{Eq. wt. of zinc}}$$

$$\therefore \quad \frac{w_1}{w} = \frac{\text{Eq. wt. of copper}}{32 \cdot 75} \qquad [\text{Eq. wt. of Zn is known} = 32 \cdot 75]$$

$$\therefore \text{ Eq. wt. of Cu} = \frac{w_1 \times 32 \cdot 75}{w}$$

(6) **Electrolytic method.**

Principle : When electricity is passed through a solution of a metallic salt, the weight of the substance deposited or liberated at the cathode or anode is related to its equivalent weight by the following equation—

$$W = \frac{E.c.t}{F}$$

Where,

W = Weight of the substance liberated in g.
E = Eq. wt. of the substance
c = Current in ampere
t = time in seconds
F = Faraday or 96500 coulombs

$$\text{or, } E = \frac{W \times F}{c \times t}$$

This relation is deduced on the basis of Faraday's laws of electrolysis.

For details of the process, see chapter on Electrolysis.

[B] Determination of Equivalent weight of non metals.

(1) Equivalent weight of oxygen :

Pure and dry CuO is taken in a bulb tube and weighed.

One end of the tube is connected to a weighed U-tube contaning fused $CaCl_2$. Through the other end dry H_2 gas is slowly passed in. When air inside the bulb tube is completely replaced by hydrogen gas, the bulb is heated strongly by bunsen flame (Fig 4·5). Hydrogen combines with oxygen of CuO to form H_2O which is absorbed by fused $CaCl_2$ in the U-tube. When no more H_2O is absorbed by $CaCl_2$, the apparatus is cooled in the current of hydrogen gas. The U-tube and bulb tube are detached and separately tared in a chemical balance. The bulb will lose in weight and this loss in weight corresponds to the weight of oxygen. The weight of U-tube will be increased and this increase in weight is due to the weight of water formed.

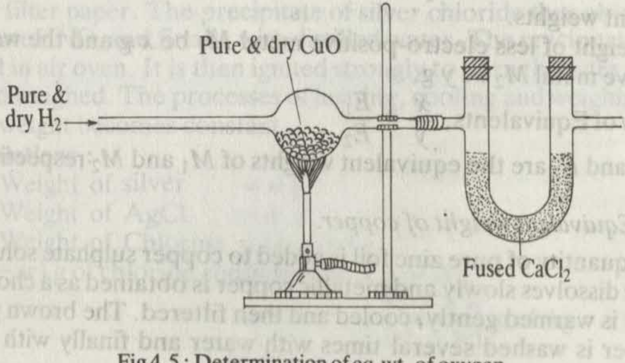


Fig 4.5 : Determination of eq.wt. of oxygen

$$CuO + H_2 = Cu + H_2O$$

Calculation :

Before expt. :

Wt. of bulb + CuO = w g

After expt. :

Wt. of bulb + Cu = w_1 g

Wt. of oxygen = $(w - w_1)$ g

Before expt. :

Wt. of U-tube containing fused $CaCl_2 = w_2$ g

After expt. :

Wt. of U-tube containing fused $CaCl_2 = w_3$ g

Wt. of water produced = $(w_3 - w_2)$ g

Wt. of hydrogen = wt. of H_2O − wt. of O_2

$= [(w_3 - w_2) - (w - w_1)]$ g = x g (say)

x g of hydrogen combine with $(w - w_1)$ g of O_2

1·008 " " " $\dfrac{(w - w_1) \times 1{\cdot}008}{x}$ g of O_2

Hence the eq. wt. of oxygen = $\dfrac{(w - w_1) \times 1{\cdot}008}{x}$

(2) Equivalent weight of carbon by oxidation method :

[A] **Principle :** A weighed quantity of pure carbon is oxidised to carbon dioxide by heating it in a current of pure and dry O_2. CO_2 thus produced is absorbed by soda lime in a U-tube. The weight of sodalime is taken. The difference between the weights of CO_2 produced and that of carbon taken, gives the weight of O_2 which has combined with the carbon. Thus, the equivalent weight of carbon is determined from the relation.

$$\text{Eq. wt.} = \frac{\text{weight of carbon taken} \times 8}{\text{weight of oxygen combined}}$$

[B] **Procedure :** About 0·2 g of pure sugar charcoal is placed in a previously weighed porcelain boat. It is weighed again with the sugar charcoal in it. The boat along with the sugar charcoal is next introduced into a hard glass combustion tube opened at both ends and nearly half of which is filled with dry CuO. The combustion tube is clamped in horizontal position. The end of the tube nearer to CuO is connected with a previously weighed U-tube containing sodalime. The U-tube contains a guard tube with fused $CaCl_2$ in it. From the other end of the tube is passed pure and dry oxygen. The porcelain boat with sugar charcoal and the CuO are heated strongly. The charcoal is completely oxidised to CO_2. Any CO formed during oxidation of sugar charcoal is oxidised by CuO to CO_2.

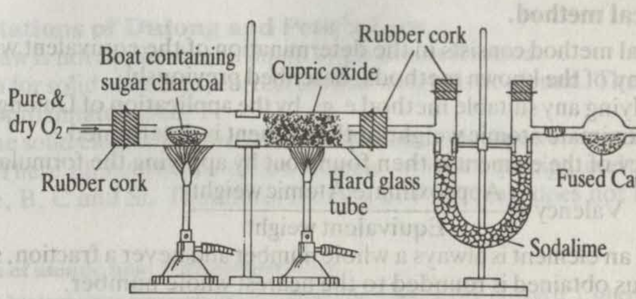


Fig 4.6 : Determination of eq.wt. of carbon

$$CuO + CO = Cu + CO_2$$

The stream of oxygen is continued till whole of CO_2 is swept away from the tube into the U-tube where it is absorbed by sodalime. The tubes are carefully detached and weighed.

Calculation :

Wt. of porcelain boat = a g

Wt. of boat + sugar charcoal = b g

$\therefore$ Wt. of sugar charcoal = $(b - a)$ g

After expt., wt. of U-tube = c g

Before expt., wt. of U-tube = d g

$\therefore$ Wt. of $CO_2 = (c - d)$ g

$\therefore$ Wt. of oxygen that combines with sugar charcoal

$$= (\text{wt. of } CO_2 - \text{wt. of charcoal})$$
$$= (c - d - b + a)\text{ g} = x \text{ g (say)}$$

Now x g of oxygen combine with $(b - a)$ g of carbon

$\therefore$ 8 " " " " $\frac{(b-a)\times 8}{x}$ g of carbon

$\therefore$ Equivalent weight of carbon $= \left[\frac{(b - a \times 8}{x}\right]$

4.5. Determination of atomic weight of element.

Various methods are available for the determination of atomic weight of an element, the chief methods are given below :

(1) **Chemical method.**
(2) **Vapour density method.**
(3) **Cannizzaro's method.**
(4) **By the application of Dulong and Petit's law.**
(5) **From molecular weight and atomicity.**
(6) **From the ratio C_p/C_v of gaseous element.**
(7) **By the application of Mitscherlich's Law of Isomorphism.**
(8) **Mass spectrograph method.**

1. Chemical method.

(i) Chemical method consists in the determination of the equivalent weight of the element by any of the known methods, described previously.

(ii) By applying any suitable method e.g., by the application of Dulong and Petit's law, the approximate atomic weight of the element is determined.

(iii) Valency of the element is then found out by applying the formula.

$$\text{Valency} = \frac{\text{Approximate Atomic weight}}{\text{Equivalent weight}}$$

Valency of an element is always a whole number and never a fraction, so the value of valency thus obtained is rounded to the nearest whole number.

(iv) Correct atomic weight of the element is obtained by multiplying equivalent weight with valency.

$$\text{Correct At. wt.} = \text{Equivalent wt.} \times \text{valency}$$

This method is illustrated in the following example—

The equivalent weight of a solid element is 9 and its specific heat is 0·208.

The approximate atomic weight of the solid element (by applying Dulong and Petit's law) $= \dfrac{6{\cdot}4}{0{\cdot}208} = 30{\cdot}77$

The valency of the element $= \dfrac{30{\cdot}77}{9} = 3{\cdot}41 \approx 3$ (nearest whole number)

The accurate atomic weight of the element $= 9 \times 3 = 27$.

2. Vapour density method :

Most of the metallic chlorides are volatile. By measuring their vapour densities, the atomic weight of the metal present in the metallic chloride can be calculated as follows :—

Let the valency and equivalent weight of an element (M) be x and E respectively.

Let the vapour density of the chloride $= v$

As the valency of the element is x, so the molecular formula of the chloride $= MCl_x$

$\therefore$ The At. wt. of the element $= E \times x$

$\therefore$ The Mol. wt. of the chloride $= Ex + 35{\cdot}5x$

$$= x(E + 35{\cdot}5)$$

$$\text{or, } x = \frac{\text{Mol. wt. of the metallic chloride}}{E + 35{\cdot}5} = \frac{2\times \text{Vap. density}}{E + 35{\cdot}5} = \frac{2v}{E + 35{\cdot}5}$$

Once x is known, it is multiplied with equivalent weight (E) to calculate exact atomic weight of the element.

i.e., the exact At. wt. $= E \times v$

3. Cannizzaro's method : Already discussed in Chapter II.

4. Dulong and Petit's Law.

In 1819, **Dulong** and **Petit** observed—*Except few elements (Carbon, Boron, Silicon and Beryllium) the atomic heat of all solid elements at room temperature are same and numerically equal to 6·4 (approximately).*

The product of atomic weight and specific heat, with a numerical value of approximately 6·4, is known as atomic heat.

$$\text{Atomic weight} \times \text{specific heat} = 6{\cdot}4 \text{ (approx.)}$$

$$\text{or, Atomic weight} = \frac{6{\cdot}4}{\text{sp. heat}} \text{(approx.)}$$

The atomic weight so recorded by applying Dulong and Petit's rule is not accurate.

- **Limitations of Dulong and Petit's Law :**

(i) The law is not applicable to liquid or gaseous elements.

(ii) Even for solid elements, correct atomic weight is not found. The method gives only the approximate value.

(iii) Some solid elements at ordinary temperature deviate very considerably from this rule. These elements are of low atomic weight and high melting point and include Be, B, C and Si. Therefore, Dulong & Petit's law does not hold for these elements.

Variation of atomic heat with temperature.

The atomic heats of some elements like beryllium (Be), boron (B), carbon (C), silicon (Si) at ordinary temperature are as follows—

Beryllium	= 3·4	Carbon	= 1·37
Boron	= 2·64	Silicon	= 4·77

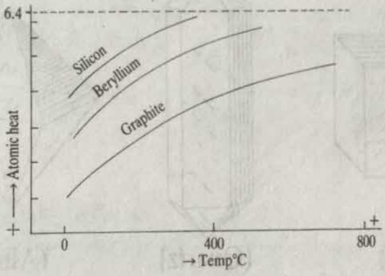


Fig 4.7 :

As shown in the following graph, those elements which obey Dulong and Petit's law must have atomic heat 6·4 (approx.) at normal temperature. For the above mentioned elements (Be, B, C, Si) the maximum value of atomic heat is reached only at high temperature. Consequently Dulong and Petit's law is obeyed by these elements, only at high temperatures.

5. From molecular weight and atomicity :

If the molecular weight and atomicity of a gaseous element are known, its atomic weight can be found out by applying the formula.

$$\text{Atomic wt.} = \frac{\text{molecular weight}}{\text{atomicity}}$$

Atomicity refers to the number of atoms per molecule.

6. From the value of C_p/C_v of a gas or vapour :

If C_p and C_v refer to the specific heats of a gas or vapour at constant pressure and at constant volume respectively then $\gamma = C_p/C_v$ is found to be constant depending upon the atomicity of a gas or vapour. Hence a knowledge of C_p/C_v gives an idea of the atomicity of the gas or vapour. It is found that for monoatomic gas $\gamma = 1{\cdot}66$, for diatomic gas it is 1·40 and lower value for a triatomic gas. Hence knowing γ, the atomicity of the gas is known. Then by dividing molecular weight by atomicity, the atomic weight of the element can be found out.

7. By applying the law of isomorphism.

Most of the solid substances possess characteristic geometrical structure or shape and it is this shape or form which characterise them.

Isomorphism : *The property by virtue of which two or more different chemical compounds exist in the same crystalline structure, so as to form 'solid solution' is called ismorphism and chemical compounds forming crystals in which geometrically similar structural units are arranged in similar ways are said to be ismorphous.*

(*Isos* = equal, morphic = form)

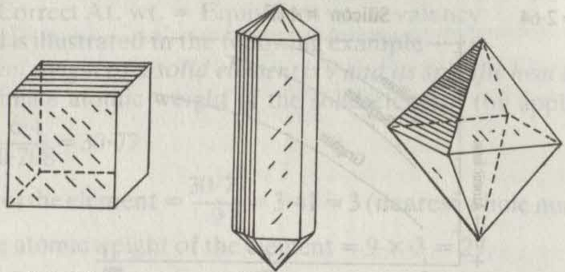
[The substances having similar crystalline structure may not be isomorphous in all cases]

• Criteria of isomorphism :

It is not always very easy to identify isomorphous substances. As a matter of fact similarity in external form is one of the features of isomorphism but not always. The chief characteristics of isomorphism are :—

(i) **Similarity in external crystalline form :**

Usually isomorphous substances have similar shapes. In some cases inspite of having identical external symmetry, the crystals have different internal structures. *If the interfacial angles, axial ratio of the crystals are identical, then they are isomorphous.*



(NaCl) (Quartz) (Alum)

Fig 4.8 :

Authentic data on the bond lengths and bond angles of a crystal are provided by X-ray crystallographic studies. Thus *alums* of general formula M'_2SO_4, $M'''_2(SO_4)_3$, $24H_2O$, where M′ stands for monovalent cation like Na^+, K^+, NH_4^+ etc., and M‴ stands for trivalent cation like Fe^{+++}, Al^{+++} or Cr^{+++} etc., are isomorphous as they exhibit same external symmetry and their interfacial angles are almost same (Fig 4.7).

(ii) **Formation of mixed crystals or solid solution :**

Whenever a saturated solution containing two or more isomorphous substances is allowed to crystallise, homogenous crystals containing all the substances are separated from the solution. Such crystals are known as mixed crystals or solid solutions, which contain two or more isomorphous compounds in the same ratio as in the solution.

Thus when a solution containing green vitriol ($FeSO_4$, $7H_2O$) and white vitriol ($ZnSO_4$, $7H_2O$) is allowed to crystallise, mixed crystals separate out which contain Fe^{++}, Zn^{++} and SO_4^{--} ions within a single crystal structure. The ratio of Fe^{++} and

Zn^{++} in the crystal will be the same as they were in the solution. Since these are single homogeneous crystals having random arrangement of Fe^{++} and Zn^{++} ions and since these are not a mixture of crystals of green vitriol and white vitriol, the term *'solid solution'* is sometimes referred to them.

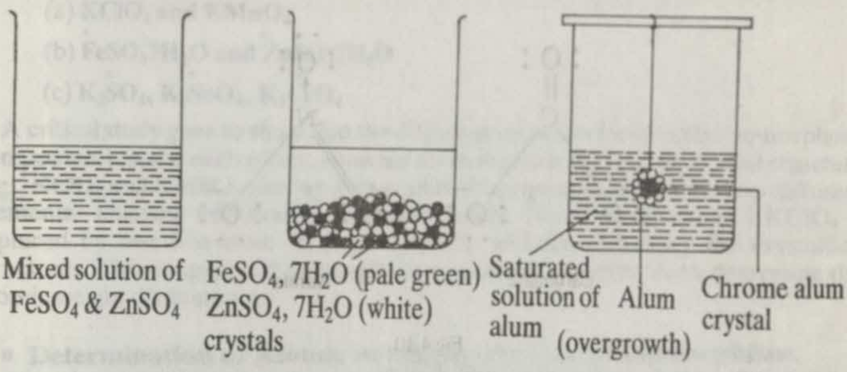

Mixed solution of $FeSO_4$ & $ZnSO_4$
$FeSO_4, 7H_2O$ (pale green)
$ZnSO_4, 7H_2O$ (white)
crystals
Saturated solution of alum
Alum (overgrowth)
Chrome alum crystal

Fig 4.9 :

(iii) **Formation of overgrowth :**

This is one of the most confirmatory test of isomorphism. A crystal of one substance (say *A*), whenever is allowed to suspend by thread into a saturated solution of another isomorphous substance (say *B*), the later deposits on *A* and as such the crystal will grow in size. Thus a crystal of colourless potash alum can be grown on the surface of a crystal of violet coloured chrome alum (Fig 4.8).

[Although formation of overgrowth is regarded as one of the best criteria of isomorphism but such overgrowth of crystals takes place depending upon structural limits. Thus since $r_{cs+} > r_{k+}$, K_2SO_4 and Cs_2SO_4 will not form overgrowth although they are isomorphous.]

- **Conditions for Isomorphism :**

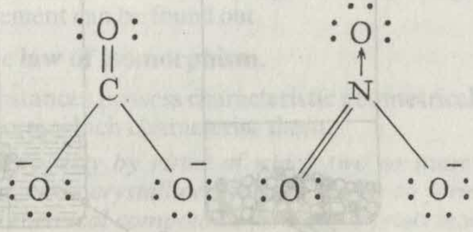
Several conditions must be fulfilled for two compounds which are isomorphous. These are—

1. The formulae of the compounds must be comparable.
2. Nature of bonding between the atoms or ions in the two crystals must be similar.
3. The relative sizes of the ions of the crystals must be very close.
4. The total number of atoms present in the isomorphous compounds must be same.
5. The cations and anions of the two crystals must be isoelectronic. In this case the isomorphous compounds may not form mixed crystals but parallel growth of the crystals must be observed.
6. The charges of the ions must be the same.

- **Examples :**

(i) **Potassium sulphate** (K_2SO_4) is isomorphous with **potassium selenate** (K_2SeO_4) but not with potassium telurate K_6TeO_6. The number of atoms in the first two cases are same but different from the third one. SO''_4 and SeO''_4 ions are tetrahedral but TeO_6^{6-} is octahedral.

(ii) $CaCO_3$ and $NaNO_3$ are isomorphous although $CaCO_3$ is insoluble in water but $NaNO_3$ is highly soluble. This is because of the fact that both CO_3'' and NO'_3 ions are isoelectronic and isostructural.



Carbonate Nitrate

Fig 4.10 :

(iii) $FeSO_4, 7H_2O$ and $CoSO_4, 7H_2O$ are isomorphous to each other. The ionic radii of both Fe^{++} and Co^{++} are very close. Both have 27 atoms, number of water molecules being same. Both of them form mixed crystal and show overgrowth.

Other examples of Isomorphous crystals :

1. White vitriol $ZnSO_4, 7H_2O$, Green vitriol $FeSO_4, 7H_2O$ and Epsom salt $MgSO_4, 7H_2O$.
2. Potash alum $K_2SO_4, Al_2(SO_4)_3, 24H_2O$ and Chrome alum $K_2SO_4, Cr_2(SO_4)_3, 24H_2O$.
3. Potassium permanganate $KMnO_4$ and Potassium perchlorate $KClO_4$.
4. K_2CrO_4 and K_2SO_4.

- **Exceptions to the law of Isomorphism :**

(1) *Sometimes compounds having different number of atoms have been found to be Isomorphous.*

e.g., $K_2SO_4, Al_2(SO_4)_3, 24H_2O$ and $(NH_4)_2SO_4, Al_2(SO_4)_3, 24H_2O$.

Silver sulphide (Ag_2S) is isomorphous with *lead sulphide* (PbS). *Barium permanganate* is isomorphous with K_2SO_4. The formula of barium permanganate being $Ba(MnO_4)_2$.

(2) *There are some substances which have same crystalline structure. Yet they are not isomorphous.* This is because (i) their formula are different, (ii) nature of bonding is entirely different, (iii) they do not form mixed crystal, (iv) they do not display the phenomenon of overgrowth. Thus Rock Salt and diamond have same crystal structure yet they are not isomorphous because while Rock Salt is ionic, diamond is a typical covalent solid.

Mitscherlich's Law of Isomorphism :

As a result of study on the crystalline phosphates and Arsenates e.g., KH_2PO_4, H_2O and KH_2AsO_4, H_2O and analogous compounds. E. Mitscherlich (1819) observed.

An equal number of atoms combined in the same manner produce the same crystalline form and that the crystalline form of a compound is independent of the chemical nature of the combined atoms and is determined only by their number and method of combination. This is known as Mitscherlich's Law of Isomorphism.

Some examples of Isomorphous substances are given here. The key elements forming isomorphous substances are given asterisk.*

(a) **$K\overset{*}{Cl}O_4$ and $K\overset{*}{Mn}O_4$**

(b) **$\overset{*}{Fe}SO_47H_2O$ and $\overset{*}{Zn}SO_47H_2O$**

(c) **$K_2\overset{*}{S}O_4$, $K_2\overset{*}{Se}O_4$, $K_2\overset{*}{Cr}O_4$**

A critical study goes to show that the different elements forming the isomorphous compounds replace each other, atom for atom without altering the crystal structure e.g., $KClO_4$ and $KMnO_4$ are two isomorphous compounds formed by two different elements—chlorine and manganese respectively. Now one Cl-atom in $KClO_4$ is replaced by one Mn-atom to form $KMnO_4$ without disturbing the crystalline structures. This property of isomorphous compounds enables us to determine the atomic weight of elements.

• Determination of Atomic weight by the Law of Isomorphism.

(1) Let the sulphate of a metal M be isomorphous with zinc sulphate. Since the formula of the later is $ZnSO_4, 7H_2O$, the formula of the metal sulphate must be $MSO_4, 7H_2O$. Since zinc sulphate contains one atom of zinc so following Mitscherlich's law, the metal sulphate must also contain 1 atom of M and its formula will be $MSO_4, 7H_2O$. Let the atomic weight of the metal be x.

$\because$ The molecular weight of $MSO_4, 7H_2O$.

$$= x + 32 + 4\times16 + 14 + 7\times16 = x + 222$$

$$\% \text{ of M in metal sulphate} = \frac{100\times x}{x+222}$$

The percentage of M in the metal sulphate is found out by actual analysis. Let it be y.

$$\therefore \frac{100\times x}{x+222} = y$$

The atomic weight of M can easily be evaluated from this equation.

(2) As isomorphous compounds have identical formulae, the ratio of the weights of two elements which combine with same weight of all other elements of the compounds, is the same as the ratio of their atomic weights. Let us consider two isomorphous compounds *AM* and *BM* where *A* and *B* are analogous elements with atomic weights *a* and *b* respectively.

Let x and y be percentage of A and B in the 2 compounds.
hence $\%\ M$ in $AM = 100 - x$
and $\%\ M$ in $BM = 100 - y$

$$\text{Weight of } A \text{ per unit weight of } M = \frac{x}{100-x}$$

$$\text{''}\quad \text{''}\ B\ \text{''}\quad \text{''}\quad \text{''}\quad \text{''}\ M = \frac{y}{100-y}$$

$$\therefore \text{ the number of atoms of } A = \left[\frac{x}{(100-x)} \times \frac{1}{a}\right]$$

$$\text{the number of atoms of } B = \left[\frac{y}{(100-y)} \times \frac{1}{b}\right]$$

Now 1 atom of *A* replaces 1 atom of *B*.

∴ No. of atoms of *A* = No. of atoms of *B*.

$$\text{or, } \frac{x}{(100-x)} \times \frac{1}{a} = \frac{y}{(100-y)} \times \frac{1}{b}$$

$$\text{or, } \frac{x}{(100-x)} \bigg/ \frac{y}{(100-y)} = a/b \text{ ......(i)}$$

Representing the equation (i) in words :—

$$\frac{\text{Weight of } A \text{ that combines with definite wt. of } M}{\text{Weight of } B \text{ that combines with definite wt. of } M} = \frac{\text{Atomic weight of } A}{\text{Atomic weight of } B}$$

Hence by knowing the percentage amounts of *A* & *B* and either *a* or *b*, the atomic weight of other element can be found out.

- **Valency from Law of Isomorphism :**

Since equal number of atoms (or constituent particles) combine together to form isomorphous compounds—hence they have similar chemical formula. Therefore the elements forming isomorphous substances must have the same valency—otherwise their chemical formulae could not have been the same. Hence if valency of one is known, the other must be known e.g., Phosphorous and Arsenic form isomorphous compounds Na_2HPO_4 and Na_2HAsO_4. Since the valency of P is 3, that of As must be 3. Again zinc sulphate and nickel sulphate are isomorphous. The valency of zinc in zinc sulphate is 2. So the formula of zinc sulphate is $ZnSO_4$, $7H_2O$, hence the valency of nickel must be 2 and the formula of nickel sulphate must be $NiSO_4$, $7H_2O$.

8. Mass spectrograph method.

Mass spectrograph introduced by F. W. Aston (1919) is a device to detect isotopes, their relative abundances and to determine their masses with an accuracy much higher than that of any method described earlier. A schematic diagram of Mass spectrograph is shown here. A narrow stream of positive ray (positive ions) is sent through two slits and then through a specially shaped electric field between two capacitor plates in which they are deflected in such a way that those ions having approximately the same kinetic energy come out in the same direction. The ions then enter a magnetic field. The deflection produced here is inversely proportional to the mass of the particle. Ions having same value of *e*/*m* (*e* = charge of the particle

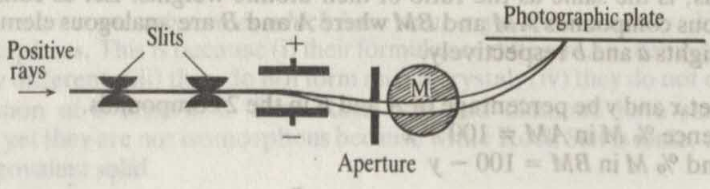


Fig 4.11 :

and m = its mass) travel along path which converge to a photographic plate where a sharp line is produced for each type of particle present in the original beam. On developing the photographic plate, a *mass spectrum* is obtained which contains line with a definite e/m value. By comparing a line given by particle of known mass, the unknown mass of a particle can be found out.

4.6. Determination of Molecular weight of a substance.

(1) From vapour density of a gas or vapour :

We know from Avogadros law,

$$\textit{Vapour density of a gas} = \frac{\text{Weight of a given volume of a gas or vapour}}{\text{Weight of same volume of hydrogen}}$$

(Under the similar conditions of temperature & pressure)

$$\textit{Mol. wt. of the gas} = 2 \times \textit{Vapour density}$$

Example :

Let the weight of 2 litres of a gas at N.T.P. be 2·88 g

We know that the weight of 1 litre of hydrogen at N.T.P. is 0·09 g

$$\therefore \text{ Vapour density of the gas} = \frac{\text{Weight of 2 litres of the gas at N.T.P.}}{\text{Weight of 2 litres of hydrogen at N.T.P.}}$$

$$= \frac{2{\cdot}88\text{ g}}{2\times0{\cdot}09\text{ g}} = 16$$

$\therefore$ Mol. wt. $= 2 \times 16 = 32$.

(2) From Graham's Law of diffusion :

See Graham's Law of diffusion in chapter seven.

(3) By the application of ideal gas equation :

For 1 mole of an ideal gas $PV = RT$

For n mole of an ideal gas $PV = nRT$

or, $PV = \frac{g}{M}RT$ Since $n = \frac{g}{M}$

Here P = Pressure of the gas in atmos, V = Volume of the gas in litre, T = Temp. of the gas in Kelvin scale, R = Universal gas constant, g = Weight of the gas in gram, M = Molecular weight of the gas.

Thus a knowledge of weight of a given volume of a gas at known temperature and pressure enables us to calculate its molecular weight.

Example :

Let the weight of 600 ml of a gas kept in a gas jar at 400 mm pressure and 20°C be 0·866 g.

Here $P = \frac{400}{760}$ atmos, $T = 273 + 20 = 293\text{K}$

$V = 0{\cdot}6$ litre, $R = 0{\cdot}082$ litre atmos K^{-1} mole^{-1}

$$\therefore M = \frac{g.R.T.}{P.V.} = \frac{0{\cdot}866 \times 0{\cdot}082 \times 293 \times 760}{400 \times 0{\cdot}6}$$

$$= 65{\cdot}89$$

$\therefore$ Molecular weight of the gas $= 65{\cdot}89$

(4) Beckmann's process (for non volatile solute) :

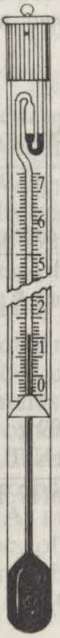


Fig 4.12 : Beckman's thermometer

The molecular weight of non volatile solutes like *urea, glucose* can be easily evaluated by using Beckman thermometer which is designed to record small changes in temperature.

Raoult's Law of elevation of boiling point or depression of freezing point suggests that, the boiling point of a solution is always higher than that of the pure solvent but freezing point of a solution is less than that of the pure solvent when a non-volatile solute is dissolved in it.

A special type of thermometer known as Beckmann's thermometer records the change of temperature during the dissolution of a given weight of solute in a given volume of solvent. Then by applying the following two formulae, the molecular weight of the non volatile solid can be found out.

If M_2 = Molecular weight of the solute
$\triangle T_b$ = Elevation of boiling point of the solution.
W_1 = Weight of solvent in g.
W_2 = Weight of solute in g.
K_b = Molal elevation constant.

$$\triangle T_b = K_b \frac{W_2 \times 1000}{W_1 \times M_2}$$

Similarly if K_f = Molal depression constant
$\triangle T_f$ = Depression of freezing point of the solution. The other symbols being same significance as before.

$$\triangle T_f = K_f \frac{W_2 \times 1000}{W_1 \times M_2}$$

Example : *When 2·130 g of Iodine are dissolved in 60·28 g of diethyl ether, the boiling point of the resulting solution is increased by 0·296°C. Given K_b of ether = 2·11. Find the molecular weight of Iodine.*

Ans : Here $\triangle T_b = 0{\cdot}296$, $W_2 = 2{\cdot}130$ g, $W_1 = 60{\cdot}28$ g, $K_b = 2{\cdot}11$
Applying the formula,

$$\triangle T_b = K_b \cdot \frac{W_2 \times 1000}{W_1 \times M_2}$$

$$0{\cdot}296 = \frac{2{\cdot}11 \times 2{\cdot}13 \times 1000}{60{\cdot}28 \times M_2}$$

$$\text{or, } M_2 = 251{\cdot}9$$

or, Molecular weight of Iodine = 251·9.

(5) From Raoult's law of relative lowering of vapour pressure :

Whenever a non volatile solute is dissolved in a solvent to form a dilute solution, it is always observed that the vapour pressure of the solution becomes less than that of the pure solvent. Based on this observation *Raoult Law* states—*The relative lowering of the vapour pressure of a solution containing a non volatile solute is equal to the mole fraction of the solute in the solvent.*

Let P_0 = vapour pressure of the pure solvent
P = vapour pressure of the pure solution.

$\therefore$ The relative lowering of vapour pressure $= \dfrac{P_0 - P}{P_0}$

Again let n_2 = number of moles of solute and n_1 = number of moles of solvent

Mole fraction of solute $x = \dfrac{n_2}{n_1 + n_2}$

Applying Raoult's law

$$\frac{P_0 - P}{P_0} = \frac{n_2}{n_1 + n_2} = x$$

For very dilute solution, $n_1 + n_2 \approx n_1$, *then*

$$\frac{P_0 - P}{P_0} = \frac{n_2}{n_1}$$

$$\text{or, } \frac{\text{Vap. pressure of solvent} - \text{Vap. pressure of solution}}{\text{Vap. pressure of solvent}} = \frac{\text{Number of moles of solute}}{\text{Number of moles of solvent}}$$

Let w g of a solute of molecular weight m is dissolved in W g of a solvent of molecular weight M

$$\text{then } n_2 = \frac{w}{m} \text{ and } n_1 = \frac{W}{M}$$

$$\text{or, } \frac{P_0 - P}{P_0} = \frac{w/m}{W/M}$$

By applying the above formula the molecular weight of the solute can be easily found out.

4.7. Determination of Molecular weight by Victor Meyer's method.

This is the most convenient method for determining the molecular weight of volatile liquid in the laboratory.

[A] Principle :

In this method a known weight of a volatile liquid is vaporised rapidly by raising the temperature well above its boiling point. The produced vapours are made to displace an equal volume of air which is collected over water and is measured. The volume of displaced air thus obtained is reduced to N.T.P.

The volume of displaced air at N.T.P. corresponds to the volume of vapour of the liquid.

Let the volume of the vapour at N.T.P. be V ml and the weight of which is w g.

$$\therefore \text{ The vapour density of the vapour} = \frac{\text{wt. of } V \text{ ml vapour at N.T.P.}}{\text{wt. of } V \text{ ml } H_2 \text{ at N.T.P.}}$$

$$= \frac{\text{wt. of } V \text{ ml vapour at N.T.P.}}{V \times 0{\cdot}000089 \text{ g}}$$

$$= \frac{w}{V \times 0{\cdot}000089}$$

$$\therefore \text{ The molecular wt. of the liquid} = 2 \times \text{Vap. density} = 2 \times \frac{w}{V \times 0{\cdot}000089}$$

[B] Apparatus :

(i) Victor Meyer tube, (ii) Copper jacket for heating the liquid, (iii) Hofmann's bottle, (iv) Eudiometer tube for collecting the gas.

[C] Description of Victor Meyer tube :

The Victor Meyer tube consists of a long glass tube having a bulb at the bottom and a side tube near the top. The free end of the side tube dips under water in a trough. The upper end of the tube is fitted with a rubber cork. The Victor Meyer tube is placed inside an outer copper jacket. The copper jacket contains a suitable liquid whose boiling point is atleast 20°C—30°C above the boiling point of the experimental liquid. This temperature is much above the boiling point of the liquid whose molecular weight is to be determined. A little glass wool is placed inside the Victor Meyer tube. This prevents the cracking of the tube as well as the Hofmann's bottle when the bottle is dropped into the tube.

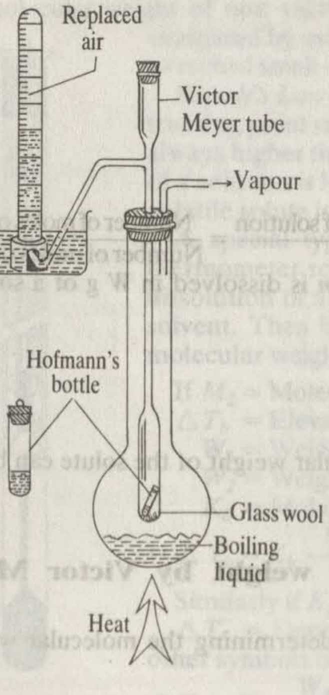


Fig 4.13 :

[D] Procedure : The Victor Meyer tube is first cleaned and dried and the apparatus is set up in the copper jacket by means of a rubber cork. The jacket is provided with an outlet for the escape of the vapours of the liquid taken in it. The free end of the side tube in Victor Meyer tube is immersed in water in a trough. Now, the liquid in the copper jacket is continuously boiled, when air inside the Victor Meyer tube expands and bubbles out of water in the trough. When a steady temperature is reached i.e., when the air inside the tube ceases to expand, no more air bubble will be found to come out of the water in the trough. Now a graduated eudiometer tube filled with water is inverted over the free end of the side tube. A Hofmann's bottle is weighed. It is then filled with a suitable quantity of the experimental liquid (0·2 to 0·5 g) and weighed again.

The rubber stopper is now removed and the Hofmann's bottle containing the experimental liquid is dropped into the Victor Meyer tube and the rubber stopper is quickly replaced. The higher temperature due to the boiling liquid in the outer copper jacket vaporises the liquid in the Hofmann's bottle. The produced vapours of the experimental liquid push out an equal volume of air from the tube which collects in the eudiometer tube displacing equal volume of water.

When no more air collects in the eudiometer tube, it is taken out closing the open end with the thumb. The tube is next placed into a tall jar containing water. The surface of water inside and outside the tube is then brought to the same level. The volume of air is recorded. The atmospheric pressure and room temperature are also noted.

Calculations :

Let the volume of displaced air be x ml. This corresponds to the volume of the vapour obtained from the liquid in the tube at room temperature.

Temperature of the room = t°C
Barometric pressure = P mm
Aqueous tension at t°C = f mm.
The pressure of dry air = $(P - f)$ mm.
The weight of the experimental liquid = w g.

Let the volume of the vapour at N.T.P. be V ml.

$$\therefore \frac{760 \times V}{273} = \frac{(P-f)\times x}{273+t}$$

$$\text{or, } V = \frac{(P-f)\times x \times 273}{760 \times (273+t)} = y \text{ ml (say)}$$

(i) The vapour density of the liquid $= \dfrac{\text{weight of } y \text{ ml of vapour}}{\text{weight of } y \text{ ml of hydrogen}}$ (at N.T.P.)

$$= \frac{w}{y \times 0\cdot000089}$$

$\therefore$ Molecular weight of the liquid $= 2 \times \dfrac{w}{y \times 0\cdot000089}$

(ii) weight of y ml. vapour at N.T.P. $= w$ g.

" " 22400 " " " $= \dfrac{w \times 22400}{y}$ g

$\therefore$ Molecular weight $= \dfrac{w \times 22400}{y}$

(iii) The pressure of the vap. in atmos $= \dfrac{P-f}{760}$

The volume of vapour at t°C $= x$ ml $= \dfrac{x}{1000}$ litre

Temperature $= (273 + t)$K

Weight of vapour = weight of the liquid $= w$ g.

$R = 0\cdot082$ litre atmos. K^{-1} mole^{-1}.

Applying these values in ideal gas equation—

$$M = \frac{g.R.T}{P.V}, \text{ or, } M = \frac{w \times 0\cdot082 \times (273+t) \times 760 \times 1000}{(P-f)\times x}$$

Victor Meyer's method is the most convenient method for measuring vapour densities of volatile liquids but the results are not very accurate. The method is not applicable to those liquids which suffer dissociation under heat or at their boiling points.

4.8. Numerical examples.

[A] Calculation involving equivalent weight :

1. *0·2 g magnesium reacts with dil. H_2SO_4 to yield 200 ml of hydrogen at 15°C and 751·5 mm pressure. If the atomic weight of Mg be 24·38 what is the equivalent weight and valency of Mg ? Given aq. tension at 15°C = 13·55 mm.*

Ans : Pressure of dry H_2 gas $= 751\cdot5 - 13\cdot5 = 738$ mm.

Let V be the volume of hydrogen at N.T.P.

$$\therefore \frac{760 \times V}{273} = \frac{738 \times 200}{273 + 15}$$

$$\text{or, } V = \frac{273 \times 738 \times 200}{760 \times 288} = 184\cdot095 \text{ ml.}$$

The weight of 22400 ml hydrogen at N.T.P. = 2 g

The weight of 184·095 ml hydrogen at N.T.P. $= \dfrac{2 \times 184\cdot095}{22400} = 0\cdot0164$ g

$\therefore$ The equivalent weight of Mg $= \dfrac{0\cdot2}{0\cdot0164} = 12\cdot19$

$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent weight}} = \frac{24{\cdot}38}{12{\cdot}19} = 2$$

∴ Valency of Mg = 2

2. *The equivalent weight of a metal is 9. What volume of H_2 will be liberated by treating 2·7 g of the metal with HCl at 27°C and 760 mm pressure ?*

Ans : As the equivalent weight of the metal is 9,

∴ 9 g of the metal displace 11200 ml H_2 at N.T.P.

$$2{\cdot}7\text{ g} \;\;,,\;\;,,\;\;,,\;\;,,\;\; \frac{11200 \times 2{\cdot}7}{9} = 3360 \text{ ml of } H_2 \text{ at N.T.P.}$$

Let V ml be the volume of hydrogen at 27°C and 760 mm pressure.

$$\frac{760 \times V}{300} = \frac{760 \times 3360}{273} \quad \text{or,} \;\; V = 3692{\cdot}3 \text{ ml}$$

Volume of H_2 = 3692·3 ml

3. *0·218 g of a metal is dissolved in dil. HCl. The volume of H_2 liberated at N.T.P. reacts with 75 ml of O_2 at N.T.P. Calculate the equivalent weight of the metal.*

Ans : Under the same conditions of temperature and pressure 2 ml H_2 combine with 1 ml O_2

∴ 75 ml of O_2 combine with 75 × 2 = 150 ml of H_2

∴ Wt. of 150 ml of H_2 at N.T.P. = 150 × 0·000089 = 0·0134 g.

0·0134 g H_2 is replaced by 0·218 g of the metal

$$\therefore 1\text{ g} \;\;,,\;\;,,\;\;,,\;\;,,\;\; \frac{0{\cdot}218}{0{\cdot}0134} = 16{\cdot}3 \text{ g}$$

∴ The equivalent weight of the metal = 16·3

4. *0·109 g of a metal is dissolved in dil. HCl. The hydrogen thus evolved is mixed with 27·84 ml O_2 at 27°C and 750 ml pressure and the mixture is exploded. The volume of unreacted hydrogen is 27·84 ml at the same conditions of temperature and pressure. What is the equivalent weight of the metal ?*

Ans : Let the volume of O_2 at N.T.P. be V ml

$$\frac{760 \times V}{273} = \frac{750 \times 27{\cdot}84}{300} \quad \text{or,} \; V = 25 \text{ ml}$$

∴ At N.T.P. 25 ml of O_2 will combine with 2 × 25 = 50 ml of hydrogen

∴ Volume of H_2 used in explosion = 50 ml

Unreacted hydrogen = 27·84 ml at 750 mm pressure and 27°C

The volume of this H_2 at N.T.P. = 25 ml

∴ The volume of H_2 displaced by 0·109 g of metal at N.T.P. = 50 + 25 = 75 ml

∴ At N.T.P. weight of metal displaced by 11200 ml

$$= \frac{0{\cdot}109 \times 11200}{75} = 16{\cdot}27 \text{ g}$$

∴ The equivalent weight of the metal = 16·27

5. *When 2·0 g of lead are completely oxidised in air, the weight of oxide is 2·1544 g. Calculate the equivalent weight of lead.* *(W.B.H.S. '60, '70)*

Ans : Weight of O_2 = 2·1544 − 2·0 = 0·1544 g

0·1544 g of oxygen combines with 2 g of Pb

$$8 \;\;,,\;\;,,\;\;,,\;\;,,\;\;,,\;\; \frac{2 \times 8}{0{\cdot}1544} = 103{\cdot}6 \text{ g of lead}$$

∴ The equivalent weight of Pb = 103·6

6. *A metal forms two oxides. The first oxide contains 30% of oxygen. 2·88 g of the second oxide contains 0·64 g of oxygen. Calculate the equivalent weight of the metal in the two oxides. Find the valency of the metal in the two oxides if the atomic weight of the metal is 56.*

Ans : The first oxide contains 30% oxygen.

∴ Percentage of metal = (100 − 30) = 70

In the first oxide—

30 g of oxygen combine with 70 g of metal

$$8 \text{ " \quad " \quad " \quad "} \quad \frac{70 \times 8}{30} = 18{\cdot}66 \text{ g of metal}$$

∴ The equivalent weight of the metal in the 1st oxide is 18·66.

$$\text{Valency} = \frac{\text{At.wt}}{\text{Eq.wt}} = \frac{56}{18{\cdot}66} = 3$$

In the second oxide—

Weight of oxygen = 0·64 g

Weight of metal = (2·88 − 0·64) = 2·24 g

0·64 g of oxygen combine with 2·24 g of the metal

$$8 \text{ g of oxygen combine with } \frac{2{\cdot}24 \times 8}{0{\cdot}64} = 28 \text{ g}$$

∴ The equivalent weight of the metal in the second oxide = 28.

$$\text{Valency} = \frac{\text{At.wt}}{\text{Eq.wt}} = \frac{56}{28} = 2$$

7. *1·986 g of copper on oxidation give 2·47 g of cupric oxide. Again 0·346 g of metallic zinc displaces 0·335 g of metallic copper from $CuSO_4$ solution. Calculate the Eq. wt. of zinc.* *(W.B.H.S. '81)*

Ans : Weight of O_2 that combines with 1·986 g of Cu = (2·47 − 1·986) = 0·484 g.

Now 0·484 g of oxygen combines with 1·986 g of copper

$$8 \text{ g of oxygen combine with } \frac{1{\cdot}986 \times 8}{0{\cdot}484} = 32{\cdot}82 \text{ g of Cu}$$

∴ The equivalent weight of copper = 32·82

According to the law of equivalents :—

$$\frac{\text{Weight of zinc}}{\text{Weight of copper}} = \frac{\text{Eq. wt. of zinc}}{\text{Eq. wt. of copper}}$$

$$\text{or,} \quad \frac{0{\cdot}346}{0.335} = \frac{\text{Eq. wt. of zinc}}{32{\cdot}82}$$

$$\text{or, Eq. wt of Zn} = \frac{0{\cdot}346 \times 32{\cdot}82}{0{\cdot}335} = 33{\cdot}897$$

∴ The equivalent weight of Zn=33·897.

8. *The gaseous product obtained by the complete reduction of 0·3975 g of copper oxide by pure and dry H_2 is passed through previously weighed anhydrous $CaCl_2$ tube. As a result the weight of the tube is increased by 0·09 g. Find the equivalent weight of copper.* *(W.B.H.S. '64)*

Ans : $CuO + H_2 = Cu + H_2O$

The increase in weight of $CaCl_2$ tube is due to the absorption of steam.

∴ Weight of steam = 0·09 g

We know 18 g of water contain 16 g of O_2

$$0{\cdot}09 \text{ g of water contains } \frac{16 \times 0{\cdot}09}{18} = 0{\cdot}08 \text{ g of } O_2$$

This oxygen comes from 0·3975 g CuO

∴ Wt. of Cu = (0·3975 − 0·08) = 0·3175 g.

Now 0·08 g of O_2 combines with 0·3175 g of Cu.

$$8\text{ g of }O_2\text{ combine with }\frac{0{\cdot}3175\times 8}{0{\cdot}08}=31{\cdot}75\text{ g of Cu}$$

∴ The equivalent weight of copper = 31·75

9. *0·4905 g of AgCl is precipitated when a few drops of HNO_3 and $AgNO_3$ solution are added to 0·2 g of a metallic chloride solution. If the atomic weight of the metal is 23, calculate the equivalent weight of the metal. Write the formula of its oxide.*

Ans : The molecular weight of AgCl = 108 + 35·5 = 143·5

143·5 g AgCl contain 35·5 g of chlorine

$$0{\cdot}4905\text{ g of AgCl contains }\frac{35{\cdot}5\times 0{\cdot}4905}{143{\cdot}5}=0{\cdot}1213\text{ g of }Cl_2$$

0·2 g of metallic chloride must contain 0·1213 g of chlorine.

∴ Weight of metal in 0·2 g of metallic chloride = 0·2 − 0·1213 = 0·0787 g.

$$\text{The equivalent weight of the metal}=\frac{0{\cdot}0787\times 35{\cdot}5}{0{\cdot}1213}=23{\cdot}03$$

$$\text{Valency}=\frac{23{\cdot}0}{23{\cdot}03}=1$$

If M be the symbol of the metal, then the formula of its oxide = M_2O.

10. *Excess of $AgNO_3$ solution is added to 1·11 g solution of a metal chloride. The precipitated AgCl is filtered, washed and dried. The weight of AgCl is 2·87 g. Find the eq. wt. of metal.*

Ans : Let the eq. wt. of the metal be x.

We know,

$$\frac{\text{Weight of metal chloride}}{\text{Weight of silver chloride}}=\frac{\text{Eq. wt. of metal chloride}}{\text{Eq. wt. of silver chloride}}$$

$$\text{or, }\frac{1{\cdot}11}{2{\cdot}87}=\frac{x+35{\cdot}5}{108+35{\cdot}5}\quad\text{or, }\frac{1{\cdot}11}{2{\cdot}87}=\frac{x+35{\cdot}5}{143{\cdot}5}$$

$$\text{or, }x+35{\cdot}5=\frac{143{\cdot}5\times 1{\cdot}11}{2{\cdot}87}=55{\cdot}5$$

or, x = 55·5 − 35·5 = 20.

∴ The equivalent weight of the metal = 20.

11. *1·00 g of a bivalent metal carbonate is strongly heated. The weight of metal oxide is 0·6682 g. Calculate the equivalent weight and atomic weight of the metal.*

Ans : Let the symbol of the metal is M.

$$\underset{1{\cdot}00\text{ g}}{MCO_3}\xrightarrow{\Delta}\underset{0{\cdot}6682\text{ g}}{MO}+CO_2\ [M=\text{bivalent}]$$

Weight of CO_2 = (1·00 − 0·6682) = 0·3318 g

0·3318 g of CO_2 is obtained from 1·00 g of MCO_3

$$22\text{ g of }CO_2\text{ are obtained from }\frac{1{\cdot}00\times 22}{0{\cdot}3318}=66{\cdot}30\text{ g of }MCO_3$$

∴ Eq. wt. of MCO_3 = 66·30.

Now, eq. wt. of MCO_3 = Eq. wt. of M + Eq. wt. of CO_3''

$$66{\cdot}30=\text{Eq. wt. of M}+30\qquad(\text{Eq. wt. of }CO_3''=\frac{60}{2}=30)$$

∴ Eq. wt. of metal = 66·30 − 30 = 36·30

Since valency of metal = 2,
At wt. of the metal = 36·30 × 2 = 72·60.

12. *280 ml of CO_2 at N.T.P. are obtained when 1·0537 g of a bivalent metal carbonate are heated in a hard glass test tube. Calculate the eq. wt. of the metal.*

Ans : We know that the weight of a substance that gives 22·0 g of CO_2, is the eq. wt. of substance.

Weight of 22400 ml CO_2 at N.T.P. = 44 g.

$$\text{,, } \text{,, } 280\text{ ml ,, ,, ,,} \quad \frac{44 \times 280}{22400} = 0{\cdot}55\text{ g}$$

$$\frac{\text{Weight of metallic carbonate}}{\text{Weight of } CO_2} = \frac{\text{Eq. weight of metallic carbonate}}{\text{Eq. weight of } CO_2}$$

Let M be the symbol of the metal

$\therefore$ Formula of the metallic carbonate = MCO_3.

$$\text{or, } \frac{\text{Weight of } MCO_3}{\text{Weight of } CO_2} = \frac{\text{Eq. wt. of M} + \text{Eq. wt. of } CO_3''}{\text{Eq. wt. of } CO_2}$$

$$\text{or, } \frac{1{\cdot}0537}{0{\cdot}55} = \frac{\text{Eq. wt. of M} + 30}{22}$$

or, Eq. wt. of M = 12·148.

13. *When metallic magnesium reacts with 0·098 g of an acid, it forms 0·12 g of anhydrous magnesium salt. Calculate the equivalent weight of the acid if the atomic weight of Mg = 24 and valency = 2.*

Ans : Equivalent weight of Mg = 24/2 = 12.

The equivalent weight of the acid = Eq. wt. of hydrogen + Eq. wt. of acid radical
(Let eq. wt. of acid radical be x)

$\therefore$ Eq. wt. of the acid = $1 + x$

The magnesium salt consists of magnesium and the acid radical.

$\therefore$ The eq. wt. of magnesium salt = Eq. wt. of Mg + Eq. wt. of acid radical = $12 + x$

Again,

$$\frac{\text{Weight of the acid}}{\text{Weight of the Mg-salt}} = \frac{\text{Eq. wt. of the acid}}{\text{Eq. wt. of the Mg-salt}}$$

$$\text{or, } \frac{0{\cdot}098}{0{\cdot}12} = \frac{1+x}{12+x}$$

$$\text{or, } \frac{49}{60} = \frac{1+x}{12+x} \qquad \text{or, } 60 + 60x = 588 + 49x \quad \text{or, } x = 48$$

or, the eq. wt. of the acid radical = 48

$\therefore$ Eq. wt. of the acid = Eq. wt. of hydrogen + Eq. wt. of acid radical = 1 + 48 = 49.

14. *A metal M of equivalent weight 30 combines with chlorine to form a metal chloride. Calculate the weight of the metal in gram that combine with 700 ml of chlorine measured at 30°C and 560 mm pressure. Given aqueous tension at 30°C = 31·70 mm.*

Ans : Let the volume of 700 ml of chlorine be V ml at N.T.P.

$$\therefore \frac{760 \times V}{273} = \frac{(560 - 31{\cdot}7) \times 700}{273 + 30}$$

$$\text{or, } V = \frac{(560 - 31.7) \times 700 \times 273}{(30 + 273) \times 760}$$

$$= \frac{528{\cdot}3 \times 700 \times 273}{303 \times 760} = 438{\cdot}4\text{ ml}$$

As the eq. wt. of the metal is 30

11200 ml of chlorine at N.T.P. combine with 30 g of metal

$438{\cdot}4$ " " " " " " " $\dfrac{30 \times 438{\cdot}4}{11200} = 1{\cdot}17428$ g of metal

∴ Weight of the metal = 1·17428 g

[B] Calculations involving atomic weight :

15. *The specific heat of a solid metal is 0·031 cal K^{-1} $mole^{-1}$. 4·0 g of oxygen combine with 25·9 g of the metal. Find the atomic weight of the metal.* *(I.I.T. 1967)*

Ans : From Dulong and Petit's law—

Approx atomic weight of the metal = $\dfrac{6{\cdot}4}{0{\cdot}031} = 206{\cdot}45$

Now, 4·0 g of oxygen combine with 25·9 g of the metal

8 " " " " " $\dfrac{25{\cdot}9 \times 8}{4} = 51{\cdot}8$ g of the metal

∴ Eq. wt. of the solid metal = 51·8

Valency = $\dfrac{206{\cdot}45}{51{\cdot}8} = 3{\cdot}9 = 4$. Since valency is a whole number.

∴ Correct atomic weight of the element = 51·8 × 4 = 207·2.

16. *1·003 g of a metallic sulphide on being strongly heated yield 0·242 litre of SO_2 at 27°C and 690 mm pressure. If the specific heat of the metal is 0·0498 cal K^{-1} $mole^{-1}$ what is the atomic weight of the metal ?*

Ans : According to Dulong and Petit's law,

the approx. atomic weight of the metal = $\dfrac{6{\cdot}4}{0{\cdot}0498} = 128{\cdot}5$

Let the volume of SO_2 at N.T.P. be *V* litre.

∴ $\dfrac{760 \times V}{273} = \dfrac{690 \times 0{\cdot}242}{300}$ or, $V = 0{\cdot}1999$ litre = 199·9 ml

We know, 22400 ml of SO_2 at N.T.P. weigh 64 g

199·9 " " " " " $\dfrac{64 \times 199{\cdot}9}{22400} = 0{\cdot}5712$ g

Again 64 g of SO_2 contain 32 g of sulphur.

0·5712 " " " " $\dfrac{32 \times 0{\cdot}5712}{64} = 0{\cdot}2856$ g of sulphur

Weight of metal = 1·003 − 0·2856 = 0·7174 g

0·2856 g of sulphur combines with 0·7174 g of metal.

16 " " " " " $\dfrac{0{\cdot}7174 \times 16}{0{\cdot}2856} = 40{\cdot}2$ g of metal.

∴ The equivalent weight of the metal = 40·2

Valency of the metal = $\dfrac{128{\cdot}50}{40{\cdot}2} = 3{\cdot}19 \approx 3$

∴ Exact atomic weight of the metal = 40·2 × 3 = 120·6.

17. *A crystalline hydrated metallic sulphate contains 8·1% of metal and 43·2% of sulphate (SO_4^{--}) radical. The specific heat of the metal is 0·242 cal K^{-1} $mole^{-1}$. Find the molecular formula of the hydrate.* *(I.I.T. '77)*

Ans : The eq. wt. of $SO_4^{--} = 96/2 = 48$

43·2 parts by weight of SO_4^{--} radical combine with 8·1 parts by weight of metal.

∴ 48 " " " " SO_4^{--} " " " $\dfrac{8{\cdot}1 \times 48}{43{\cdot}2} = 9$ parts by weight of metal.

∴ The equivalent weight of the metal = 9

The approx. at. wt. of the metal = $\frac{6\cdot4}{0\cdot242} = 26\cdot44$

Valency of the metal = $\frac{26\cdot44}{9} = 2\cdot93 \approx 3$

∴ Exact at. wt. of the metal = 9 × 3 = 27
Let x be the number of water of crystallisation
∴ Formula of the hydrate :— $M_2(SO_4)_3 . xH_2O$
∴ Percentage of water of crystallisation in the metallic sulphate
$= [100 - (43\cdot2 + 8\cdot1)] = 48\cdot7$
The sulphate contains 2 atoms of the metal *M*.
1 gram atomic wt. of the metal = 27 g of metal
2 gram atomic wt. of the metal = 54 g of metal
8·1 g of metal combine with 48·7 g of water
54 " " " " " $\frac{48\cdot7 \times 54}{8\cdot1} = 324\cdot7$ g of water

Number of moles of water = $\frac{324\cdot7}{18} \approx 18$

Hence the formula of the hydrate sulphate $M_2(SO_4)_3.18H_2O$

18. *The chloride of a metal contains 54·4% of chlorine. The vapour density of the chloride is 8·16 (O = 1). Find out the eq. wt. valency and atomic wt. of the metal. Give the formula of the metallic chloride.*

Ans : % of metal in the chloride = 100 − 54·4 = 45·6%

Eq. wt. of the metal = $\frac{45\cdot6 \times 35\cdot5}{54\cdot4} = 29\cdot757$

The vapour density of the metallic chloride = 8·16 (O = 1)
The vapour density of oxygen = 16
∴ The vapour density of the chloride (H = 1) = 8·16 × 16 = 130·56
∴ Molecular weight of the metallic chloride = 130·56 × 2 = 261·12
Let x be the valency of the metal.
∴ Formula of the metallic chloride = MCl_x
At. wt. of the metal = $29\cdot757x$
Mol. wt. of the metallic chloride = $29\cdot757x + 35\cdot5x$
or, $29\cdot757x + 35\cdot5x = 261\cdot12$
or, $x \approx 4$ (nearest whole number)
Hence the correct atomic weight of the metal = 29·757 × 4 = 119·03
Formula of the chloride = MCl_4.

19. *The percentage of metal in a metallic sulphate is 20·9%. The metallic sulphate is isomorphous with $ZnSO_4.7H_2O$. What is the atomic weight of the metal.*
(Delhi S.S.S.E. 1987)

Ans : Since the metallic sulphate is isomorphous with $ZnSO_4.7H_2O$, its formula will be $MSO_4.7H_2O$ (M = Symbol of the metal).

Let x be the atomic weight of the metal.
∴ Mol. wt. of the metallic sulphate = $x + 32 + 64 + 7 \times 18 = x + 222$
Now, $(x + 222)$ parts by wt. of the metallic sulphate contain x parts by wt. of the metal
∴ 100 " " " " " " " " " $\frac{x \times 100}{x + 222}$ " " " " "

According to the given data,—

$\frac{x \times 100}{x + 222} = 20\cdot9$ or, $100x = 20\cdot9x + 20\cdot9 \times 222$ or, $x = 58\cdot65$

∴ The atomic weight of the metal = 58·65

20. *Both magnesium sulphate and zinc sulphate are isomorphous. Magnesium sulphate contains 9·75% of Mg and 39·02% of SO_4^{--} ion. Zinc sulphate contains 22·6% of Zn and 36·5% of SO_4^{--} ion. Find the atomic weight of Mg if the atomic weight of zinc be 65.*

Ans : 9·75 parts by weight of Mg combine with (100 − 9·75) = 90·25 parts by weight of other elements present in $MgSO_4$.

Again 22·6 parts by weight of Zn combine with (100 − 22·6) = 77·4 parts by weight of other elements present in $ZnSO_4$

or, 90·25 parts by weight of other elements combine with $\frac{22·6 \times 90·25}{77·4} = 26·35$ parts by weight of zinc.

∴ 90·25 parts by weight of other elements combine with 9·75 parts by weight of Mg and 26·35 parts by weight Zn. Since the two sulphates are isomorphous, both Mg and Zn will occur in these two sulphates in the ratio of their atomic weights.

$$\therefore \frac{9·75}{26·35} = \frac{\text{At. wt. of Mg}}{\text{At. wt. of Zn}} \quad \text{or,} \quad \frac{9·75}{26·35} = \frac{\text{At. wt. of Mg}}{65}$$

$$\therefore \text{At. wt. of Mg} = \frac{65 \times 9·75}{26·35} = 24·05$$

Atomic weight of Magnesium is 24·05

21. *0·24 g of a metal liberated 82·2 ml H_2 at N.T.P. when reacted with dil. H_2SO_4. After the reaction was over, the solution was allowed to crystallise. A white crystal was separated which was found to be isomorphous with $FeSO_4.7H_2O$. The crystal contains 23% of the metal. Calculate the correct atomic weight of the metal.*

Ans : The weight of 82·2 ml H_2 at N.T.P. = $\frac{2·016 \times 82·2}{22400} = 0·007398$ g

0·007398 g of H_2 is displaced by 0·24 g of metal

∴ 1·008 " " " " " $\frac{0·24 \times 1·008}{0·007398} = 32·7$ g of the metal

Hence the Equivalent weight of the metal = 32·7

Since the metallic sulphate is isomorphous with $FeSO_4.7H_2O$, the formula of the metallic sulphate is $MSO_4.7H_2O$.

Let x be the atomic weight of the metal.

∴ Mol. wt. of the sulphate = $x + 32 + 64 + 7 \times 18 = x + 222$

According to the problem—

$$\frac{x \times 100}{x + 222} = 23 \quad \text{or,} \quad x = 66·3$$

∴ Atomic weight of the metal = 66·3 (approximate)

The valency of the metal = $\frac{66·3}{32·7} = 2$

The exact at. wt. of the metal = 32·7 × 2 = 65·4.

22. *The oxides of two metals X and Y are isomorphous. The atomic weight of X is 43·5 and the vapour density of its chloride is 75. The oxide of Y contains 40% oxygen. Calculate the atomic weight of Y.*

Ans : The molecular weight of the chloride of $X = 75 \times 2 = 150$

Let v be the valency of X. The formula of its chloride = XCl_v

Its molecular weight = $43·5 + 35·5v$

$$43·5 + 35·5v = 150$$

$$35·5v = 106·5 \quad \text{or,} \quad v = 3$$

Hence the formula of the oxide of $X = X_2O_3$

The oxide of Y contains $(100 - 40) = 60\%$ of Y

$\therefore$ Equivalent weight of $Y = \frac{60 \times 8}{40} = 12$

Since the two oxides are isomorphous,

$\therefore$ the formula of the oxide of Y is Y_2O_3 and the valency of Y is also 3

$\therefore$ the atomic weight of $Y = 12 \times 3 = 36$.

23. *If the equivalent weight of a metal (M) be x and the formula of its oxide be M_mO_n, show that the atomic weight of the metal* $= \frac{2xn}{m}$. *(W.B.H.S.'83, '92)*

Ans : Let a be the atomic weight of M.

From the formula of M_mO_n, the mol. wt. of it $= ma + 16n$

$16n$ parts by weight of oxygen combine with ma parts by weight of metal

8 " " " " " " $\frac{ma \times 8}{16n} = \frac{ma}{2n}$

Hence the eq. wt. of the metal $= \frac{ma}{2n}$

Given the eq. wt. of the metal $= x$

$\therefore \frac{ma}{2n} = x$ or, $ma = 2xn$ or, $a = \frac{2xn}{m}$ i.e., atomic weight $= \frac{2xn}{m}$

24. *When 2·0 g of a trivalent metal react with silver nitrate solution, 24·0 g of metallic silver are deposited. What is the atomic weight of the metal ? How much copper will be deposited when 4·0 g of the metal react with $CuSO_4$ solution (Given eq. wt. of silver = 108)* *(Senior Cambridge, '70)*

Ans : According to the law of equivalents,

$$\frac{\text{Weight of the metal}}{\text{Weight of silver}} = \frac{\text{Equivalent weight of the metal}}{\text{Equivalent weight of silver}}$$

or, $\frac{2 \cdot 0}{24 \cdot 0} = \frac{\text{Eq. wt. of the metal}}{108}$

$\therefore$ Equivalent weight of the metal $= \frac{108 \times 2}{24} = 9$

Hence the atomic weight of the metal $= 9 \times 3 = 27$

Again by applying the law of equivalents,

$\frac{4}{\text{Wt. of copper}} = \frac{9}{31 \cdot 7}$

$\therefore$ Wt. of copper $= \frac{4 \times 31 \cdot 7}{9} = 14 \cdot 1$

$\therefore$ Weight of copper deposited $= 14 \cdot 1$ g.

25. *The chloride of a metal M contains 52·75% of chlorine. 0·1 g of this metal M is displaced by 0·088 g of another element N. Calculate the eq. wt. of both M and N. If the valency of N be 2, what is its atomic weight ?*

Ans : The chloride of M contains $(100 - 52 \cdot 75) = 47 \cdot 25\%$ of M

Equivalent weight of $M = \frac{47 \cdot 25 \times 35 \cdot 5}{52 \cdot 75} = 31 \cdot 79$

Now, $\frac{\text{Weight of } M}{\text{Weight of } N} = \frac{\text{Eq. wt. of } M}{\text{Eq. wt. of } N}$

or, $\frac{0 \cdot 1}{0 \cdot 088} = \frac{31 \cdot 79}{\text{Eq. wt. of N}}$ or, Eq. wt. of N $= 27 \cdot 97$

Its atomic weight $= 2 \times 27 \cdot 97 = 55 \cdot 94$.

26. *The atomic weight of a metal is 86. A piece of this metal weighing roughly 0·40 g, liberated 112 ml of dry hydrogen from dil. H_2SO_4 at N.T.P. What is the exact weight of the metal dissolved in the acid.*

Ans : The approximate equivalent weight of the metal $= \dfrac{11200 \times 0{\cdot}40}{112} = 40$

$$\text{Valency of the metal} = \frac{86}{40} = 2{\cdot}15 \approx 2$$

$$\therefore \text{The exact eq. wt. of the metal} = \frac{86}{2} = 43.$$

43 g of the metal liberate 11200 ml of H_2 at N.T.P.

$$\therefore \text{The weight of the metal dissolved} = \frac{112 \times 43}{11200} = 0{\cdot}43\text{ g}$$

27. *On complete vaporisation in a Victor Meyer tube, 0·185 g of a liquid displaced 56 ml of air at N.T.P. Calculate the mol. wt. of the liquid.* *(Joint Ent '83, I.I.T. '84)*

Ans : 0·185 g of the liquid is converted into 56 ml vapour at N.T.P.

$\therefore$ Weight of 56 ml vapour at N.T.P. is 0·185 g

$$\text{Weight of 22400 ml vapour at N.T.P.} = \frac{0{\cdot}185 \times 22400}{56} = 74\text{ g}$$

$\therefore$ Molecular weight of the liquid = 74.

28. *Calculate the molecular weight of a substance, 0·4 g of which when dissolved in 20 g of benzene lowers its freezing point by 0·75 K. Molar freezing point depression constant K_f for benzene is 5·1 K molality^{-1}.* *(A.I.S.S.C.E. 1988)*

Ans : Here wt. of solute = 0·4 g, wt. of solvent = 20 g

Depression of freezing point $\triangle T_f = 0{\cdot}75$ K, $K_f = 5{\cdot}1$ K

Applying Raoult's Law of depression of freezing point,

$$\text{Molecular weight } (M) = K_f \, \frac{\text{Weight of solute} \times 1000}{\text{Weight of solvent} \times \triangle T_f}.$$

$$M = \frac{5{\cdot}1 \times 0{\cdot}4 \times 1000}{0{\cdot}75 \times 20} = 136$$

Hence molecular weight of the susbtance is 136.

29. *A solution containing 18 g of a solute per litre of solution gave an osmotic pressure of 2·39 atmosphere at 27°C. Calculate the molecular weight of the solute.* *(Delhi board 1988)*

Ans : Applying ideal gas equation—

$$M = \frac{\text{weight of solute} \times R \times T}{PV}$$

Weight of solute = 18 g $\qquad V = 1$ litre

Osmotic pressure $P = 2{\cdot}39$ atmosphere $\qquad T = 273 + 27 = 300$ K

$$M = \frac{18 \times 0{\cdot}082 \times 300}{2{\cdot}39 \times 1} = 185{\cdot}27$$

Hence the molecular weight of the solute = 185·27

30. *At 25°C, 36 g of a mono saccharide dissolved in 1000 g of water lowered the vapour pressure by 0·0614 mm of Hg. The vapour pressure of water at 25°C is 17·5391 mm of Hg. Calculate the molecular weight of the substance.*

Ans : Applying Raoult's Law of the relative lowering of vapour pressure—

$$\frac{P_o - P}{P_o} = \frac{n}{N} = \frac{wM}{Wm}$$

P_o = Vapour pressure of pure solvent = 17·5391 mm

P = Vapour pressure of solution
$\therefore\ P_o - P$ = Lowering of vapour pressure = 0·0614 mm
w = Weight of the solute = 36 g
W = Weight of the pure solvent = 1000 g
M = Molecular weight of the solvent = 18
m = Molecular weight of the solute

$$\text{or, } m = \frac{wM}{W} \times \frac{P_o}{P_o - P} = \frac{36 \times 18}{1000} \times \frac{17{\cdot}5391}{0{\cdot}0614} = 185{\cdot}1$$

Hence the molecular weight of the substance = 185·1.

• Exercises •

1. Define equivalent weight and gram equivalent weight of an element. *[H.S. '82, '93 (T) '81]*

2. Deduce a relation between the atomic weight, equivalent weight and valency of an element and hence show that equivalent weight of an element may vary.

3. What is gram equivalent weight ? What is the difference in expressing chemical equivalent and gram-equivalent ? *[Jont. Ent. '81]*

4. 'The equivalent weight of an element is constant'—justify the statement.

The equivalent weights of two elements *A* and *B* are same, but the atomic weight of *B* is twice that of *A*—how could you explain this ? *[H.S. '83]*

5. (a) State the condition under which the equivalent wt. and atomic wt. of an element have the same value ;

(b) Is the equivalent weight of iron in ferrous oxide and ferric oxide same ?

(c) 'The equivalent weight of an element depends on the reaction it undergoes'—explain the statement with illustrations.

6. 'Hydrogen displacement method of determination of equivalent weight of metals, is applicable for a few metals'.—What are the characteristics of such metals ? Describe the principle of this method. Explain why this method is not applicable in determining the equivalent weights of sodium and copper.

7. Explain why in the determination of equivalent weight of zinc by hydrogen displacement method— (i) the process is not carried out in a Woulfe's bottle, (ii) the weight of zinc taken should be in between 0·08 g and 0·1 g, (iii) excess of H_2SO_4 must be used, (iv) few drops of $CuSO_4$ solution are added before adding acid, (v) the piece of zinc in the beaker is covered by an inverted funnel, (vi) to measure the volume of H_2 in the eudiometer tube, the level of water inside and outside the tube is brought to the same level and during this operation the tube is held with a piece of paper and not with the fingers, (vii) aqueous tension at the room temperature should be noted.

8. 'The equivalent weight of an element changes with the change of its oxidation number'—Explain the statement giving suitable example. *[H.S. '83]*

9. Explain why the equivalent weights of Mg, Cu and Ag are determined by H_2 displacement method, oxidation method and formation of chloride method respectively ?

10. Describe the methods for determining the equivalent weights of sodium and silver. Explain why the equivalent weights of alkali metals are determined from their chloride salts indirectly.

11. Describe the method of determining the equivalent weight of copper starting from pure metallic copper. *[H.S. '83]*

12. Describe the method of determining the equivalent weights of carbon and oxygen ?

13. Prove that the atomic weight of an element is equal to or a simple multiple of its equivalent weight.

14. (a) Define atomic heat of an element. *[Joint Ent. '84 H.S. ,89]*

(b) State Dulong and Petits Law. What are its limitations ?

(c) Dulong and Petit's law is approximately correct, yet the exact atomic weight of an element can be determined with its help.—Explain. *[H.S. '93]*

15. State the law of equivalent proportions. Show that the law of reciprocal proportions is a corrolary of the law of equivalent proportions. *[Joint Ent. '79]*

17. What are isomorphous substances ? What is isomorphism ? What are the criteria of isomorphism ? *[Joint Ent. '79]*

18. The equivalent weight of a metal *M* is *E* and the formula of its oxide is M_xO_y. Show that the valency and atomic weight of the metal *M* are $2y/x$ and $2y\,E/x$ respectively.

19. State Dulong and Petit's law. How is this law applied to find out the atomic weight of an element. What are the limitations of this method ? *[H.S. '91]*

20. Describe how the molecular weight and vapour density of a volatile liquid are determined by Victor Meyer's method ?

21. Molecular weight of which type of compounds can be determined by Victor Meyer's method ? [*H.S.* '*93*]

22. In the Victor Meyer's method for the determination of molecular weight of a volatile liquid compound, why it is unwise to take large quantity of such liquid substance ? [*H.S.* '*90*]

- **Numerical problems :**

1. Determine the equivalent weight of each of the following compounds, assuming the formula weight of these compounds as X, Y and Z respectively.
(i) Na_2SO_4 ; (ii) $Na_3PO_4\,12H_2O$; (iii) $Ca_3(PO_4)_2$. [***Ans.*** $\frac{x}{2}, \frac{y}{3}, \frac{z}{6}$] [*MLNR '91*]

2. Find the equivalent weight of H_3PO_4 in the reaction $Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2H_2O$.
(At. wt. P = 31, Ca = 40) [***Ans.*** 49] [*I.I.T.* '*82*]

3. Find the equivalent weight of potassium chlorate and potassium iodate in the following equations—
(i) $ClO_3^- + Fe^{2+} + H^+ \rightarrow Cl^- + Fe^{3+} + H_2O$
(ii) $IO_3^- \rightarrow ICl$. [***Ans.*** 20·416, 53·5]

4. Find the equivalent weight of $KMnO_4$ in the following reaction—
(i) $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$
(ii) $2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$

5. 0·4 g of a metallic oxide contains 0·16 g of oxygen. What is the equivalent weight of the metal ? [***Ans.*** 12]

6. 3·1439 g of ferric chloride is obtained from 1·0813 g of iron. Calculate the equivalent weight and valency of iron in this compound (Fe = 55·85, Cl = 35·5) [***Ans.*** 18·637, 3]

7. Find the volume of H_2 produced at NTP when 1·45 g of a metal is treated with excess of dilute sulphuric acid. The equivalent weight of the metal is 9. [***Ans.*** 1·804 litre]

8. 0·109 g of Mg on being treated with dil HCl evolves 109·1 ml of moist H_2 at 17°C and 754·5 mm pressure. Find the equivalent weight of Mg. (aqueous tension at 17°C = 14·4 mm) [***Ans.*** 12·345]

9. The solid residue which was obtained by the action of nitric acid on 0·6842 g of pure metallic copper was strongly heated, when 0·8567 g of black residue is obtained. Calculate the gram equivalent weight of coper. [***Ans.*** 31·73 g]

10. The complete combustion of a solid element in *x* ml of O_2 yields *x* ml of gaseous oxides under the same conditions of temperature and pressure. The vapour density of the gaseous oxide is 22. Find the equivalent weight of the element. [***Ans.*** 3]

11. 0·1903 g of a metallic carbonate on being treated with dil H_2SO_4 yields 0·2589 g of dry sulphate. What is the equivalent weight of the metal ? [***Ans.*** 19·93]

12. 0·1827 g of the chloride of a metal is quantitatively converted into 0·1057 g of its oxide. Calculate the equivalent weight of the metal (Cl = 35·5) [***Ans.*** 29·74]

13. 0·362 g of a metal displaces 3·225 of silver form a solution of silver nitrate. What is the equivalent weight of the metal ? (Ag = 107·8 and valency = 1) [***Ans.*** 12·1]

14. When $AgNO_3$ solution is added to 1 g KCl, 1·926 g of AgCl is obtained. The equivalent weight of Ag = 108 and that of Cl_2 = 35·5. What is the equivalent weight of potassium. [***Ans.*** 39·01]

15. 1·02 g of a metal formed 1·31 g of its oxide. The specific heat of the metal is 0·056. Find its exact atomic weight. [***Ans.*** 112·56] [*H.S.* '*89*]

16. The oxide of solid element contains 10·3 percent of oxygen by weight. The specific heat of the element is 0·0305 cal degree^{-1} g^{-1}. Find out the correct atomic weight of the element. [***Ans.*** 208·98] [*H.S.* '*90*]

17. The chloride of a metal contains 20·2% metal. The specific heat of the metal is 0·224. Calculate the exact atomic weight of the metal and write down the molecular formula of chloride of the metal. [***Ans.*** 26·95 ; MCl_3] [*H.S.* '*91*]

18. The oxide of a metal contains 53·3% of O_2. The vapour density of its chloride is 85 (H = 1). Find the equivalent weight, valency, atomic weight and formula of the oxide of the metal. [***Ans.*** 7·01, 4, 28·04, MO_2]

19. The chloride of a metal contains 58·65 percent of chlorine. The vapour of the chloride is 91 times heavier than the same volume of H_2 at NTP. Find the equivalent weight, atomic weight and valency of the metal. [***Ans.*** 25·028, 75·084, 3]

20. 65·4 g of a metal on being reacted with acid liberate 22·4 litres of H_2 at NTP. The vapour density of its chloride is 68·2. Determine the equivalent weight and atomic weight of the metal. [***Ans.*** 32·7, 65·4]

21. H_2 gas is passed over heated cupric oxide when its weight decreased by 59·784 g and the weight of produced water 67·28 g. What is the equivalent weight of O_2. [***Ans.*** 8·039]

22. 0·51 g of $AgNO_3$ is required for complete precipitation of chlorine from 0·275 g of a metallic chloride. The specific heat of the metal is 0·057. Find the atomic weight of the metal. [***Ans.*** 112·32]

23. The chloride of a metal contains 29·34% of Cl_2. The chloride salt is isomorphous with KCl. Calculate the atomic weight of the metal. [***Ans.*** 85·5]

24. A compound (*X*) contains 28·2% of K and 25·6% of Cl_2 and the rest is O_2. Another compound (*Y*) which contains 24·7% of K, 34·8% of Mn and rest is O_2. *X* is isomorphous with *Y*. Find the atomic weight of Mn. [***Ans.*** 55·06]

25. In the two isomorphous salts Cu_2S and Ag_2S the percentages of S are 20·14 and 12·94 respectively. The atomic weight of Cu = 63·57. Calculate the atomic weight of silver. [***Ans.*** 107·9]

26. The sulphate of a metal is isomorphous with $MgSO_4$, $7H_2O$. 0·6538 g of the metal replaces 2·16 g of Ag from $AgNO_3$ solution. Find the atomic weight of the metal. [***Ans.*** 65·38]

27. 1·02 g of a metallic oxide contains 0·54 g of metal. Find equivalent weight and atomic weight of the metal. The atomic heat of the metal is 0·216 cal deg^{-1}. [***Ans.*** 9 and 27] [*H.S. '84*]

28. Ferrous sulphate combines with ammonium sulphate to form a mixed sulphate which is isomorphous with $CuSO_4$, $(NH_4)_2SO_4$, $6H_2O$. The weight of $FeSO_4$ present in the mixed sulphate is exactly 19/7 part of iron present in the mixed sulphate. Find the atomic weight of iron. [***Ans.*** 56]

29. 0·1306 g of a metal reacts with dil. H_2SO_4 to liberate 45 ml of H_2 at NTP. The residue after evaporation yields a crystal which is isomorphous with $FeSO_4$, $7H_2O$. The molecular weight of the sulphate is 287. Calculate the atomic weight of the metal. [***Ans.*** 65·2] [*H.S. '66*]

30. 0·06 g of a metal reacts with dil. H_2SO_4 to liberate 20·55 ml of H_2 at NTP. The salt obtained after the reaction on evaporation and cooling yields a crystal which is isomorphous with $FeSO_4$, $7H_2O$. Find the equivalent weight and exact atomic weight of the metal. [***Ans.*** 32·7, 65·4] [*H.S. '86*]

31. Prove from the following data, that mercury is monoatomic—

(i) 20 g of Hg combine with 1·6 g of O_2.
(ii) 50 ml of mercury vapour at NTP weigh 0·44615 g.
(iii) The specific heat of mercury is 0·033.

32. 0·0623 g of a volatile liquid on being vaporised in a Victor Meyer's apparatus displaces 31·5 ml of air which is collected by the displacement of water at 15°C and 750 mm pressure. Aqueous tension at 15°C = 12·7 mm. Find the molecular weight of the liquid. [***Ans.*** 48·3]

33. 0·1 g of a volatile liquid on vaporisation in a Victor Meyer's tube 27 ml of moist air are displaced at 15°C and 740 mm pressure. Aqueous tension at 15°C = 12·7 mm. Calculate the molecular weight of the liquid. [***Ans.*** 91·41]

34. The oxides of two metals *M* and *N* are isomorphous. The atomic weight of *M* is 52 and the vapour density of its chloride is 79. The oxide of *B* contains 47·1% of O_2. Find the atomic weight of *B*. [***Ans.*** 26·9]

35. The green coloured oxide of chromium is isomorphous with iron oxide. The oxide contains 68·43% by weight of chromium. Calculate the correct atomic weight of chromium. [***Ans.*** 52·02] [*Jt. Ent. '90*]

36. 0·05 g of a liquid hydrocarbon was burnt completely in excess of dry oxygen. The contraction observed on cooling the residual gas mixture after combustion was 40 cc. In a Victor Meyer's experiment, 0·2 g of the vapour of same hydrocarbon displaces 53·3 cc of dry air at NTP. Calculate the molecular formula of the hydrocarbon. [***Ans.*** C_6H_{12}] [*Jt. Ent. '90*]

37. The equivalent weight of an element is 13·16. It forms an acidic oxide which reacts with KOH to form a salt which is isomorphous with K_2SO_4. Calculate the atomic weight of the element. [***Ans.*** 78·96]

38. 1·0 g of Acid when reacts with Mg yields 1·301 g of magnesium salt. Find out the equivalent weight of the acid. [***Ans.*** 36·54]

39. 5·01 g of a metallic oxide on reduction by hydrogen produce 4·41 g of the metal. The specific heat of the metal is 0·055. What is the atomic weight of the metal ? [***Ans.*** 117·6] [*W.B.H.S. '93*]

40. 10 g of an element A combines with 25 g of another element B. The equivalent weight of A being 20, find the equivalent weight of B. [***Ans.*** 50] [*W.B.H.S. '94*]

41. 20 g of a metal on reaction with dil H_2SO_4 liberates 0·504 g of H_2. How much metallic oxide will be produced from 2 g of the metal ? [***Ans.*** 2·4 g] [*W.B.H.S. '97*]

42. Two 10 gram bars of two metals (at wt. A_1 and at wt A_2) are heated to 60°C and then immersed in identical insulated containers each containing 200 g of water at 20°C. Which metal will cause a greater temperature rise in water ? Given $A_1 > A_2$. [***Ans.*** Second bar of at. wt. A_2] [*W.B.J.E. '97*]

5

ACIDS, BASES AND SALTS

Introduction.

In the earliest days of experimental chemistry it had been observed that calcareous earths, such as lime stone ($CaCO_3$), gave effervescence when dissolved in certain solvents like vinegar. Moreover, dilute solutions of such solvents possessed a characteristic sour taste. Because of this property, they were called **acids** (*"Acetum"* means vinegar). Another class of compounds was also recognised, the properties of which are completely different from acids. These are called **bases.** They were first isolated from the ashes of various plants and were given the name—***alkali*** (Arabic word *ALQILI* means ashes of a plant). Acids have a sour taste, while bases have a characteristic bitter taste. Bases can destroy the properties of acids when mixed with them.

5.1. Acids.

[A] Classical concept of acids :

Acids : *An acid is a compound the molecule of which contains one or more replaceable hydrogen atoms, a part or whole of which may be replaced by a metal or a group of elements acting like a metal to produce salt.*

An acid turns blue litmus red, possesses a sour taste and gives hydrogen ions in aqueous solution and reacts with alkali to produce salt and water.

[B] Arrhenius concept of acids :

The first mechanistic picture of acid-base properties of compounds came to light when the *theory of electrolytic dissociation* was put forward by Arrhenius. According to **Arrhenius**—*An acid is a compound which when dissolved in water dissociates to produce hydrogen ions (H^+) as the only positively charged ions or cations.*

Examples : **Acid** **Cation** **Anion**

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$$

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{---}$$

(i) It should be mentioned that pure H^+ ion (bare proton) cannot exist in free state in aqueous medium. This is because of the fact that H^+ ion produces hydroxonium ion $(H_3O)^+$ by combining with one molecule of water.

$$H^+ + H_2O \rightleftharpoons H_3O^+ + 256 \text{ k cals mole}^{-1}$$

As the heat of hydration of the above reaction is very high, H_3O^+ is very stable in aqueous medium.

(ii) According to **Fajan's rule,** an H^+ ion is very minute and hence have a strong tendency to go into the covalent state by combining with an H_2O molecule to form $(H_3O)^+$ ion.

In the light of above discussion, Arrhenius idea of acid may be stated as follows :

"An acid is a substance which gives rise to $(H_3O)^+$ (Hydroxonium ion) in aqueous solution. In other words, acidic solutions are formed by a chemical reaction in which an acid transfers a proton to water."

$$HCl + H_2O \rightleftharpoons (H_3O)^+ Cl^- \rightleftharpoons (H_3O)^+ + Cl^-$$
$$H_2SO_4 + 2H_2O \rightleftharpoons 2(H_3O)^+ SO_4^{--} \rightleftharpoons 2(H_3O)^+ + SO_4^{--}$$

Limitations of Arrhenius theory : According to the concept of Arrhenius, acids exhibit their acidic properties only in aqueous solution. In fact, in absence of water or in benzene and in other covalent solvents, anhydrous HCl can not turn blue litmus red. Anhydrous vapour of HNO_3 can not liberate CO_2 from $CaCO_3$—which is a characteristic property of all acids.

It has now been proved that acid-base reactions take place in non aqueous solvents also. Some acid base reactions are there which take place without any solvent, e.g., $HCl\,(g) + NH_3\,(g) = NH_4Cl\,(s)$.

5.2. Properties of acids.

(i) **Change of colour of the indicator :** The aqueous solution of an acid turns blue litmus red and turns methyl orange from orange to red.

(ii) **Reactions with metals :** Metals which are above hydrogen in the electro chemical series (Mg, Zn, Al, Fe etc.), displace the replaceable hydrogen of the acid and liberate hydrogen.

$$Zn + H_2SO_4 = ZnSO_4 + H_2 \uparrow$$

(iii) **Reactions with bases :** Acids react with bases to produce salt and water.

$$\begin{array}{llll} \text{Acid} & + \text{ base} & = \text{Salt} & + \text{ water} \\ HCl & + NaOH & = NaCl & + H_2O \\ H_2SO_4 & + MgO & = MgSO_4 & + H_2O \end{array}$$

(iv) **Reactions with carbonates and bicarbonates :** Metallic carbonates and bicarbonates react with acids producing effervescence due to the liberation of carbon dioxide.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 \uparrow + H_2O$$
$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + CO_2 \uparrow + H_2O$$

(v) Aqueous solution of acids imparts $(H_3O)^+$ ions. Consequently all acids in aqueous medium conduct electric current. Pure HCl being a covalent compound cannot conduct electricity but becomes a good conductor of electricity when dissolved in water.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

• All acids contain hydrogen but all hydrogen containing compounds are not acids.

According to the classical theory all acids must contain hydrogen but all compounds containing hydrogen are not acids. A compound containing one or more hydrogen atoms in its molecule is termed as an acid only when its hydrogen atom or atoms are replaced by a metal or by a group of elements behaving like a metal producing salt. The compounds containing hydrogen, like NH_3, PH_3, CH_4 etc., do not produce H_3O^+ ions in aqueous medium. The hydrogen atoms of these compounds are not replaced by metals. They do not react with bases to produce salt and water, and so these compounds are not called acids. On the other hand though water contains hydrogen atoms which can be replaced by some metals, yet it is not acid as it does not produce salt. Instead of salt it produces bases by its action with metals.

There are, however, various compounds which do not contain hydrogen, yet are regarded as acids—such type of compounds are better known as Lewis acid e.g., BF_3, $FeCl_3$, $AlCl_3$, BCl_3 etc.

5.3. Classification of acids.

[A] Classification according to molelcular architecture :

According to the molecular structure, acids are classified as—(i) *Hydracids,* (ii) *Oxyacids.*

(i) **Hydracids :** *The acids which contain hydrogen and other non-metallic elements or radicals, but not oxygen, are known as hydracids.*

The name of a hydracid generally begins with the prefix *'hydro'* and end with the suffix *'ic'*, e.g., hydrochloric acid (HCl), hydrocyanic acid (HCN).

(ii) **Oxyacids :** *The acids which contain one or more oxygen atom, besides hydrogen atoms, are called oxyacids.* Acidic oxides on dissolving in water produce this type of acid. They contain one or more $-OH$ groups, and other oxygen atoms are bound to central element by co-ordinate or double bonds. The proton attached to the oxygen atom ($-OH$ group) dissociates in aqueous medium, but the other hydrogen atom which is directly bonded to the central element of the oxyacids does not dissociate.

Examples : Nitric acid (HNO_3) ; Sulphuric acid (H_2SO_4) ; Perchloric acid ($HClO_4$) etc.

Oxyacids are further classified as :

(a) **"Ous" acid :** *Oxyacids having less number of the oxygen atoms are called "ous" acids.* The oxidation number of the central element is comparatively low, e.g., Nitrous acid ($H\overset{+3}{N}O_2$). The oxidation number of nitrogen atom = +3. Sulphurous acid ($H_2\overset{+4}{S}O_3$). The O.N. of S = +4.

(b) **"Ic" acids :** *Oxyacids containing larger number of oxygen atoms are called 'ic' acids.* The oxidation number of the central element is high, e.g., sulphuric acid ($H_2\overset{+6}{S}O_4$). The O.N. of S = +6 ; perchloric acid ($H\overset{+7}{Cl}O_4$). The O.N. of Cl = +7.

(c) **Hypo acids :** *The oxyacids in which the number of oxygen atom is less than the 'ous' acids, are known as hypoacids,* e.g., Hypochlorous acid (HClO), Hyposulphurous acid ($H_2S_2O_4$) etc.

(d) **Per-acids :** *Oxyacids containing more oxygen atoms than 'ic' acids, are called per-acids,* e.g., perchloric acid ($HClO_4$), periodic acid (HIO_4) etc.

The central element forming the different oxyacids is in different oxidation states. The oxidation state of the central element in the 'hypo' acid is minimum and that in per acid is maximum as shown below :

$H\overset{+1}{Cl}O$	$H\overset{+3}{Cl}O_2$	$H\overset{+5}{Cl}O_3$	$H\overset{+7}{Cl}O_4$
Hypochlorous acid	Chlorous acid	Chloric acid	Perchloric acid

The prefixes "ortho", "meta" and "pyro" are used to distinguish acids differing in the "content of water". Note that in these cases the central element of the oxyacids is in the same oxidation state e.g.,

Central Element	**Ortho-acid**	**Meta-acid**	**Pyro-acid**
Phosphorus	$H_3\overset{+5}{P}O_4$	$H\overset{+5}{P}O_3$	$H_4\overset{+5}{P}_2O_7$
Silicon	$H_4\overset{+4}{Si}O_4$	$H_2\overset{+4}{Si}O_3$	—
Boron	$H_3\overset{+3}{B}O_3$	$H\overset{+3}{B}O_2$	$H_2\overset{+3}{B}_4O_7$

Some of the hydracids and oxyacids are tabulated below :—

ACID FORMING ELEMENT	HYDRACIDS	OXYACIDS			
		HYPO	IC	OUS	PER
Chlorine	HCl Hydrochloric	HClO Hypochlorous	$HClO_3$ Chloric	$HClO_2$ Chlorous	$HClO_4$ Per-chloric
Bromine	HBr Hydrobromic	HBrO Hypobromous	$HBrO_3$ Bromic	$HBrO_2$ Bromous	$HBrO_4$ Per-bromic
Iodine	HI Hydroiodic	HIO Hypoiodous	HIO_3 Iodic	HIO_2 Iodous	HIO_4 Per-iodic
Nitrogen	—	$H_2N_2O_2$ Hyponitrous	HNO_3 Nitric	HNO_2 Nitrous	HNO_4 Per-nitric
Phosphorous	—	H_3PO_2 Hypophosphorous	H_3PO_4 Phosphoric	H_3PO_3 Phosphorous	—
Sulphur	—	$H_2S_2O_4$ Hyposulphurous	H_2SO_4 Sulphuric	H_2SO_3 Sulphurous	$H_2S_2O_8$ Persulphuric

[B] Classification according to the basicity or the number of replaceable hydrogen atoms of acids.

Basicity of acid : *The basicity of an acid is defined as the number of hydrogen ion or ions produced by one molecule of the acid on its dissociation in aqueous solution.*

$$\text{Basicity} = \frac{\text{Gram molecular wt. of an acid}}{\text{Its gram equivalent wt.}}$$

The basicity of CH_3COOH is 1 because although it contains 4 hydrogen atoms only one is replaced by metal to form salt (CH_3COONa) and in aqueous medium only one H^+ ion is formed by one molecule of the acid.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Thus it is the replaceable hydrogen but not the total number of hydrogen atoms of an acid which determines its basicity.

(i) **Monobasic acid :** *The acid, one molecule of which gives rise to one H^+ ion in aqueous medium is called monobasic acid and its basicity is said to be 1*, e.g., HCl, HBr, HI, HCN, CH_3COOH etc.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
$$HCl \rightleftharpoons H^+ + Cl^-$$

(ii) **Dibasic acid :** *The acid, one molecule of which gives two H^+ ions in aqueous medium, is called dibasic acid and its basicity is said to be 2*, e.g., H_2SO_4, H_2CO_3 $(COOH)_2$

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}, \qquad H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{--}$$

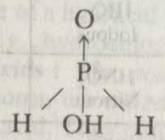
(iii) **Tribasic acid :** *The acid, one molecule of which gives three H^+ ions in aqueous medium is called tribasic acid and its basicity is said to be 3*, e.g., H_3PO_4, H_3AsO_4 etc.

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{---}$$

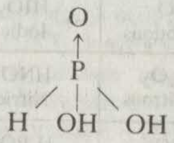
• Inspite of the presence of three hydrogen atoms in the molecule, H_3PO_2 is monobasic and H_3PO_3 is dibasic—Explain why ?

$Na_2H\ PO_3$ is a normal salt—Explain.

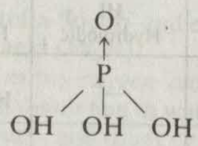
In an oxyacid the number of —OH group determines its basicity. The hydrogen atom of the —OH group is replaceable and can be replaced by metals. The hydrogen atom of the —OH group only is ionised to give H^+ ion in aqueous solution. On the other hand the hydrogen atom which is directly attached to the central element by covalent bond is not replaceable and can not produce H^+ ion in aqueous solution. Thus the basicity of an oxyacid can be known from its molecular structure. In the molecular structure of H_3PO_2 it is found that only one —OH group is present in its molecule. The other two H atoms are directly joined to P atom by covalent bond. So the H atom of —OH group can only be replaced by metals. So H_3PO_2 is monobasic.



H_3PO_2
monobasic



H_3PO_3
dibasic



H_3PO_4
tribasic

In the molecular structure of H_3PO_3 it is found that two —OH groups are present in its molecule, the other H atom is directly joined to the P atom by covalent bond and so this H atom can not be ionised. The two H atoms of two —OH groups are replaceable and so H_3PO_3 is dibasic. Thus H_3PO_3 reacts with NaOH to form Na_2HPO_3 —the two replaceable H atoms of H_3PO_3 being replaced by two Na atoms. The H atom left in the salt not being replacable, the salt is not an acid salt but a normal salt.

The structures of H_3PO_2, H_3PO_3 and H_3PO_4 explains why the formulae of their normal sodium salts are NaH_2PO_2 (sodium hypophosphite), Na_2HPO_3 (disodium phosphite), Na_3PO_4 (trisodium phosphate) respectively.

[C] Classification of acids according to the degree of ionisation.

Acids are classified as (i) *strong acid* and (ii) *weak acid* depending on their abilities to ionise in aqueous medium.

(i) **Strong acids :** *The acids which are almost completely ionised in aqueous medium producing a large number of hydrogen ions are called strong acids,* e.g., HCl, H_2SO_4, HNO_3.

(ii) **Weak acids :** *The acids which are slightly ionised in aqueous solution, and the major part of which remains as undissociated molecules, are called weak acids,* e.g., H_2CO_3, HCN, H_2S, and all organic acids.

Acetic acid (CH_3COOH) is a weak acid as in its aqueous solution, only 0·4% of it is ionised. Thus for 1000 molecules of CH_3COOH only 4 molecules dissociate to give H^+ ions.

$$\underset{996}{CH_3COOH} \rightleftharpoons \underset{4}{H^+} + \underset{4}{CH_3COO^-}$$

- **Dilute acids are stronger than concentrated acids—Explain.**

The strength of an acid depends upon the number of H^+ ions in its aqueous solution. As the number of H^+ ions increases, the strength of the acid also increases. A concentrated acid dissociates incompletely and consequently the number of H^+ ions in a concentrated acid becomes less. As a result, concentrated acid behaves like a weak acid. Thus conc. H_2SO_4 dissociates as $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

But as the acid is diluted, its degree of ionisation also increases in accordance with Arrhenius theory of electrolytic dissociation.

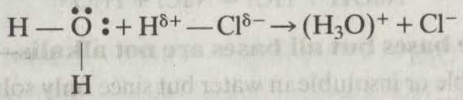
$$H_2SO_4 + 2H_2O \rightleftharpoons 2H_3O^+ + SO_4^{--}$$

Thus it is found that the number of $(H_3O)^+$ or H^+ ions in the dilute acid is much greater than that of the conc. H_2SO_4. Hence dilute acids are stronger than concentrated acids.

• Gaseous or liquid hydrogen chloride is not acidic. It does not conduct electric current but an aqueous solution of hydrogen chloride is highly acidic and conducts electric current—Explain.

Hydrogen chloride is a covalent compound. H—Cl bond contains only 17% ionic character. Hence it does not ionise to form H^+ ion. Since it does not give H^+ ion, it is neither acidic nor a conductor of electricity.

Since Cl atom is more electronegative than H atom ; the bond H—Cl is polarised as $H^{\delta+} — Cl^{\delta-}$. This in contact with water forms $(H_3O)^+$. As a result of this, the bond breaks to form $(H_3O)^+$ and Cl^-. The ions conduct electric current. The acid character of HCl is developed due to the formation of $(H_3O)^+$ ions in aqueous medium.



$$H—\underset{\underset{H}{|}}{\ddot{O}}: + H^{\delta+}—Cl^{\delta-} \rightarrow (H_3O)^+ + Cl^-$$

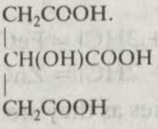
[D] Classification of acids according to source :

According to the source, acids are classified as—

(i) **Mineral acids** and (ii) **Organic acids.**

(i) Mineral acids : If the source of acid is mineral, it is commonly called mineral or inorganic acid. Thus the source of HCl is common salt NaCl, HNO_3 is nitre, H_3PO_4 is phosphorite $Ca_3(PO_4)_2$.

(ii) Organic acids : If animal or vegetable kingdom is the source of an acid it is called organic acid, e.g., citric acid



$$\begin{array}{l} CH_2COOH. \\ | \\ CH(OH)COOH \\ | \\ CH_2COOH \end{array}$$

is obtained from lemon or any citrous fruits ; Formic acid (HCOOH) is present in the sting of ant, the source of lactic acid $CH_3CH(OH)COOH$ is milk.

5.4. Base.

A base is defined as a compound, usually the oxide or the hydroxides of a metal or a group of elements acting like metal, which can neutralise an acid to produce a salt and water, e.g., ZnO, CaO, $Al(OH)_3$, Na_2O, NaOH etc.

$$ZnO + 2HCl = ZnCl_2 + H_2O$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

According to Arrhenius theory, *a base is defined as a compound which when dissolved in water gives rise to hydroxyl ions (OH^-) as the only negatively charged ion or anion.*

$$\text{base} \rightleftharpoons \text{cation} + \text{anion}$$
$$KOH \rightleftharpoons K^+ + OH^-$$
$$Na_2O + H_2O = 2NaOH \rightleftharpoons 2Na^+ + 2OH^-$$

Ammonia (NH_3) and organic amines (RNH_2) are neither oxide or hydroxide. But they are classified as base as they form salts with the acids without the formation of water.

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$
$$RNH_2 + HCl = RNH_2HCl$$

However the aqueous solution of NH_3 is basic as it forms OH^- ion in water.

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

NH_4OH is a weak base.

5.5. Alkali.

A water soluble base is called an alkali. If a base is soluble in water it turns red litmus blue. They give rise to OH^- ion in aqueous medium and reacts with acid to produce salt and water.

$$NaOH = Na^+ + OH^-$$
$$NaOH + HCl = NaCl + H_2O$$

- **All alkalis are bases but all bases are not alkalis—Explain.**

Bases may be soluble or insoluble in water but since only soluble bases are called alkalis, hence all alkalis are bases but all bases are not alkalis. Na_2O is a base. It dissolves in water to form NaOH which gives rise to OH^- ion in aqueous medium KOH, $Ca(OH)_2$, NaOH etc., are soluble in water and give rise to OH^- ions. Hence they are all alkalis.

$$Na_2O + H_2O = NaOH \qquad NaOH = Na^+ + OH^-$$
$$K_2O + H_2O = KOH \qquad KOH = K^+ + OH^-$$
$$CaO + H_2O = Ca(OH)_2 \qquad Ca(OH)_2 = Ca^{++} + 2OH^-$$

$Fe(OH)_3$, $Zn(OH)_2$, $Al(OH)_3$ are insoluble in water but they react with acids to form salt and water.

$$Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O$$
$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

These are all bases but not alkalies as they are not soluble in water and so can not ionise to give OH^- as the only anion.

- **All metallic oxides are not base—Explain.**

Most of the oxides of metals are basic but all are not so. *Metallic oxide where the oxidation number of the metal is very high, form acidic oxide* e.g., Mn_2O_7, CrO_3. They dissolve in water to form acids and react with bases or alkalis to form salts and water.

$$Mn_2O_7 + H_2O = 2HMnO_4 \quad \text{(Permanganic acid)}$$
$$CrO_3 + H_2O = H_2CrO_4 \quad \text{(Chromic acid)}$$
$$\underset{\text{acidic oxide}}{CrO_3} + \underset{\text{alkali}}{2KOH} = \underset{\text{salt}}{K_2CrO_4} + H_2O$$

5.6. Properties of Bases and Alkalis.

(i) *Alkalis and bases react with acids to produce salt and water.* One gram equivalent of an acid reacts with one gram equivalent of a base to form salt and water. This reaction is called **neutralisation reaction.**

	Base + Acid = Salt + Water
(1) Metallic oxide	$MgO + 2HCl = MgCl_2 + H_2O$ $CaO + H_2SO_4 = CaSO_4 + H_2O$ $FeO + 2HNO_3 = Fe(NO_3)_2 + H_2O$
(2) Metallic hydroxide	$KOH + HCl = KCl + H_2O$ $Mg(OH)_2 + H_2SO_4 = MgSO_4 + 2H_2O$ $Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O$
(3) Hydroxide of radical acting like metals	$NH_4OH + HCl = NH_4Cl + H_2O$ $2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$

(ii) *Bases if dissolved in water form alkalis.* This aqueous solution turns red litmus blue and turns phenolphthalein pink. The solution is slippery.

(iii) *Aqueous solution gives rise to OH^- ion* as the only anion.

$$NaOH = Na^+ + OH^-$$
$$KOH = K^+ + OH^-$$

The basic property is sometimes observed in compounds other than oxides and hydroxides, e.g., Na_2CO_3, $NaHCO_3$, NH_3, CH_3NH_2 etç. They react with acid to produce salt and water.

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

In fact they undergo hydrolysis in water giving rise to OH^- ion.

$$CO_3^{--} + H_2O \rightleftharpoons OH^- + HCO_3^-$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

5.7. Classification of Bases.

[A] Classification according to Acidity :

Acidity of a base is defined as its power of neutralising an acid. It is measured by the number of replaceable OH^- ions present in one molecule of the base or in other words, the number of OH^- ion furnished by one molecule of the base in aqueous medium is its acidity. Depending upon the acidity, bases are classified as—

(i) **Mono-acidic :** One molecule of such base gives rise to only one OH^- ion in aqueous medium e.g., NaOH, KOH etc.

$$NaOH = Na^+ + OH^-$$
$$KOH = K^+ + OH^-$$

(ii) **Di-acidic :** One molecule of such base gives two OH^- ions in aqueous medium, e.g., $Ba(OH)_2$, $Mg(OH)_2$ etc.

$$Ba(OH)_2 = Ba^{++} + 2OH^-$$
$$Mg(OH)_2 = Mg^{++} + 2OH^-$$

(iii) **Tri-acidic :** They contain three replaceable OH^- groups in the molecule, e.g., $Al(OH)_3$, $Fe(OH)_3$ etc.

If the molecule does not contain any replaceable hydroxyl group, its acidity is determined by the number of molecules of monobasic acid which is required to neutralise quantitatively one molecule of the given base.

Two molecules of HCl are required for its neutralisation by one molecule of FeO Hence the acidity of FeO is 2.

$$FeO + 2HCl = FeCl_2 + H_2O$$

Similarly, the acidity of Fe_2O_3 is 6.

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$

[B] Classification of bases according to the degree of dissociation.

According to the degree of dissociation bases are classified as (i) strong base and (ii) weak base.

(i) **Strong base :** *The base or alkali which is highly ionised in aqueous solution to produce a large number of OH^- ions, is called strong base,* e.g., NaOH, KOH, $Ca(OH)_2$ etc.

(ii) **Weak base :** *The base or alkali which is slightly ionised in water and the major portion of which exists as undissociated molecules, is known as weak base,* e.g., NH_4OH, $Cu(OH)_2$, $Al(OH)_3$ etc.

- **Other concepts of acids and bases :**

According to Arrhenius concept, acids and bases exhibit their respective properties only in aqueous medium, and bases are regarded as compounds which produce OH^- ions in aqueous solution. Thus this concept restricts bases only to water soluble bases and does not include the insoluble metal oxides as bases. It has now been proved that acid-base reactions can take place in non aqueous solvents like liquid ammonia, liquid sulphur dioxide etc. Consequently the concept of acids and bases has now been changed and the scope has been extended to include more species under the head of acids and bases.

(1) **Bronsted-Lowry concept or proton transfer concept :**

Hydrogen atom consists of one proton and one electron. When this single electron is detached, the neutral hydrogen atom is transformed into hydrogen ion which is nothing but a bare proton. Based on the transfer of proton, Bronsted and Lowry put forward a new concept of acids and bases, which was independent of the solvents. In 1923 Bronsted and Lowry proposed that—

An acid is a species (a molecule or ion) which can give up one or more protons ; i.e., an acid is a proton donor.

A base is a species (a molecule or ion) which can take up one or more protons ; i.e., a base is a proton acceptor.

According to this concept, acid-base reaction involves the donation of one or more protons by an acid and acceptance of the given up proton or protons by a base. Since an acid donates protons and a base accepts that, the reaction between acid and base may be expressed by the equation.

$$\underset{\text{(acid)}}{HA} \rightleftharpoons \underset{\text{(proton)}}{H^+} + \underset{\text{(base)}}{A^-}$$

Here we see that acid HA gives up a proton (H^+) to produce the base A^- and on the other hand the base A^- may be converted to the acid HA by accepting the proton.

Examples :

(i) CH_3COOH is acidic in water since it donates a proton to water.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Water acts as a base by accepting a proton from CH_3COOH to form H_3O^+.

$$\underset{}{\overset{\text{Acid}_1}{CH_3COOH}} \overset{+}{+} \overset{\text{base}_2}{H_2O} \overset{\rightleftharpoons}{\rightleftharpoons} \overset{\text{base}_1}{CH_3COO^-} \overset{+}{+} \overset{\text{Acid}_2}{H_3O^+}$$

(ii) When HCl is dissolved in water, HCl donates a proton to H_2O. So HCl is an acid, H_2O accepts the proton to form H_3O^+ ion. Hence H_2O is a base.

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{Cl^-}$$

(iii) In the reaction, $\underset{\text{base}_1}{NH_3} + \underset{\text{acid}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_1}{NH_4^+} + \underset{\text{base}_2}{OH^-}$

H_2O donates a proton to NH_3 and becomes OH^- and NH_3 accepts a proton from H_2O to form NH_4^+. So here H_2O acts as an acid and NH_3 acts as a base.

Thus we see that in example *(ii) water acts as a base (proton acceptor) and in example (iii) water behaves as an acid (proton donor). In the process, one molecule of water acts as an acid and the other as a base.*

$$\underset{\text{acid}_1}{H_2O} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{OH^-}$$

In liquid ammonia one molecule acts as an acid by donating proton and the other acts as a base by accepting the proton.

$$\underset{\text{acid}_1}{NH_3} + \underset{\text{base}_2}{NH_3} \rightleftharpoons \underset{\text{acid}_2}{NH_4^+} + \underset{\text{base}_1}{NH_2^-}$$

According *to this concept, an acid or a base may be neutral molecules, anion or even a cation.*

$$\underset{\text{base}_1}{HCO_3^-} + \underset{\text{acid}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_1}{H_2CO_3} + \underset{\text{base}_2}{OH^-}$$

$$\underset{\text{acid}_1}{HCO_3^-} + \underset{\text{base}_2}{NH_3} \rightleftharpoons \underset{\text{acid}_2}{NH_4^+} + \underset{\text{base}_1}{CO_3^{--}}$$

Substances like water, HCO_3^- etc., which can act both as an acid and a base are called amphoteric substance or ampholytes.

Conjugate acid base pair :

A substance produced by the loss of proton or protons from an acid is called the conjugate base of that acid.

A substance produced by the gain of a proton or protons by a base is called the conjugate acid of that base.

$$\begin{array}{ccccccc} HCl & + & H_2O & \rightleftharpoons & H_3O^+ & + & Cl^- \\ \text{acid}_1 & + & \text{base}_2 & \rightleftharpoons & \text{acid}_2 & + & \text{base}_1 \end{array}$$

In the above reaction H_3O^+ (Acid_2) is called conjugate acid of H_2O (base_2) and Cl^- (base_1) is called conjugate base of HCl (Acid_1). Thus every acid has a conjugate base formed from the acid by the loss of a proton. Similarly every base has a conjugate acid formed from the base by the addition of a proton (The word 'conjugate' means joined together as a pair or coupled).

It is observed that, the more readily an acid gives up proton, the less readily its conjugate base will take up the proton. In other words, *stronger the acid, weaker is its conjugate base and vice versa.* HCl in water is acidic because HCl is a good proton donor since its conjugate base Cl^- is weaker, i.e., has less attraction for proton than water. The proton from HCl is transferred to water to form H_3O^+. *Hence an aqueous solution of HCl is acidic.*

Special features of Bronsted Lowry theory :

(i) In every acid-base reaction there must be two conjugate acid base pairs.

(ii) An acid can exhibit its acid properties only in presence of another substance which accepts the proton. Thus HCl exhibits its acid properties in presence of water which is capable of accepting proton but it cannot exhibit its acidic properties in presence of benzene as benzene is unable to accept proton. On the other hand a base exhibits its basic properties only in presence of a proton donor substance i.e., acid.

(iii) Neutral molecules as well as ions can act as acids and bases. Thus HCl, H_2SO_4, HCO_3^-, NH_4^+, etc., are acids. This concept includes a large number of species under bases in addition to the hydroxides. Thus NH_3, Cl^-, SO_4^{--}, CH_3COO^-, NO_3^- etc., are bases.

(iv) The reaction $HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$ can not be explained as an acid-base reaction according to Arrhenius concept but can easily be explained by proton transfer concept. In this reaction the acid HCl directly transfers a proton to the base NH_3

Limitations :

This concept can be applied only to those reactions which involve proton transfer. Consequently an acid according to the concept must have an hydrogen atom which can produce H^+ ion. This concept can not explain the formation of compounds like $CaSO_4$ from CaO and SO_3 i.e., the acidic behavior of SO_3 and basic nature of CaO cannot be explained by Bronsted-Lowry concept of acids and bases.

- **The degree of ionisation of HCN is less than that of HF in water. Is the conjugate base of HCN stronger or weaker than the conjugate base of HF.—Explain.**

Acid *Base*

$$HCN \rightleftharpoons H^+ + CN^-$$
$$HF \rightleftharpoons H^+ + F^-$$

The conjugate bases of HCN and HF are CN^- and F^- respectively. Since HCN dissociates to a lesser extent than does HF, the tendency to occur the reverse reaction is greater. In the reverse reaction the conjugate base CN^- accepts a proton from water.

$$\underset{base_1}{CN^-} + \underset{acid_2}{H_2O} \rightleftharpoons \underset{acid_1}{HCN} + \underset{base_2}{OH^-}$$

or in other words CN^- is a stronger conjugate base than F^-.

(2) **Electronic concept :** According to Lewis theory of acids and bases, *an acid is a substance which can accept an unshared pair of electrons (lone pair of electrons).* All Lewis acids must contain *at least one vacant orbital where it can accept a pair of electrons from a base.*

A base is a substance that can donate a lone pair of electrons. A base must have at least one filled orbital. Again number of lone pair of electron does not indicate the strength of a base but it is the availability of lone pair of electron that determines the strength of a base. This explain why N_2 with 2 lone pairs of electron have no basic property but NH_3 with 1 lone pair of electron is a tripical base.

Neutralisation products are produced by the formation of a co-ordinate bond between a base and an acid.

Examples of Lewis acids—

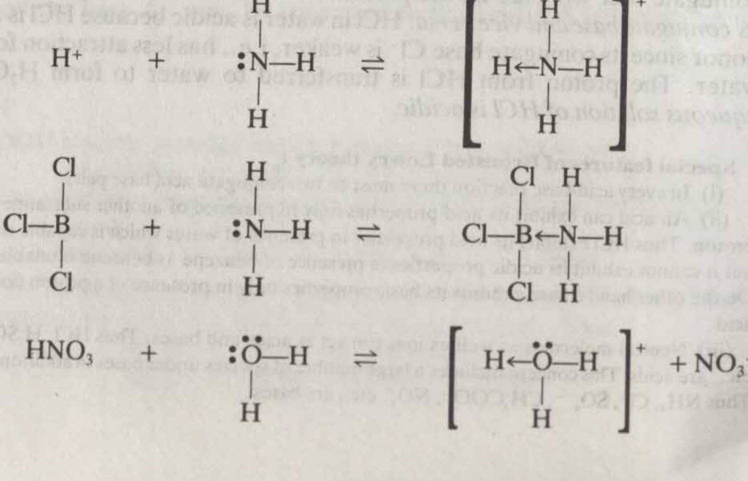
(i) *All cations* e.g., Cu^{++}, H^+, Ag^+, Fe^{++} etc.

(ii) *Some elements which contain 6 electrons in the outermost shell* e.g., S, O, Si etc.

(iii) *Electron deficient molecules* like BF_3, anhydrous $AlCl_3$, BCl_3, etc.

Lewis acids may not necessarily be protonic acids.

Acid + Base → Neutralisation Product



$$\mathrm{H^+} + :\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{N}}}-\mathrm{H} \rightleftharpoons \left[\mathrm{H}\leftarrow\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{N}}}-\mathrm{H}\right]^+$$

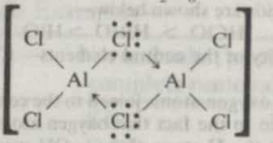
$$\mathrm{Cl}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{B}}} + :\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{N}}}-\mathrm{H} \rightleftharpoons \mathrm{Cl}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{B}}}\leftarrow\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{N}}}-\mathrm{H}$$

$$\mathrm{HNO_3} + :\underset{\mathrm{H}}{\ddot{\mathrm{O}}}-\mathrm{H} \rightleftharpoons \left[\mathrm{H}\leftarrow\underset{\mathrm{H}}{\ddot{\mathrm{O}}}-\mathrm{H}\right]^+ + \mathrm{NO_3^-}$$

$$Cu^{++} + 4\left[\begin{matrix} H \\ | \\ :N—H \\ | \\ H \end{matrix}\right] \rightleftharpoons [Cu(NH_3)_4]^{++}$$

$$H_2O + :CN^- \rightleftharpoons H \leftarrow CN + OH^-$$

- **$AlCl_3$ is a Lewis acid.** A species which contains incomplete octet of electrons can act as a Lewis acid. In $AlCl_3$ the Al atom contains incomplete octet of electrons. Thus $AlCl_3$ molecule has only 6 electrons in the valency level. As a result $AlCl_3$ molecule is capable of accepting an electron pair and act as a Lewis acid. This is exhibited in its dimeric form Al_2Cl_6.



Example of Lewis base—

All Lewis bases must have a completely filled orbital i.e., a pair of electrons with opposite spin. The pair of electrons must be loosely bonded to the nucleus of the atom. Lone pair of electrons occupying sp^3 orbital is more easily available for protonation than that of sp^2 orbital. The lone pair of sp^2 orbital is more easily available for protonation than that of sp orbital. This explains why aliphatic amines are more basic than the aromatic amines. This is because of the fact that the lone pair of electrons of nitrogen atom in aliphatic amine occurs in sp^3 hybrid orbital while the lone pair of electrons of nitrogen atom in aromatic amine occurs in sp^2 hybrid orbital.

NH_3, H_2O, RNH_2, Ether ($R - \ddot{\underset{\cdot\cdot}{O}} - R$) etc., are the examples of Lewis base.

In the reaction $CaO + SO_3 = CaSO_4$, the lone pair of electrons on the oxygen atom of CaO is donated to the sulphur atom of SO_3.

Difference between the different concepts of acids and bases in a nutshell :

Theory	Acid	Base
1. Arrhenius	Gives H^+ ions in aqueous solution as the only cations.	Gives OH^- ions in aqueous solution as the only anions
2. Bronsted Lowry	Proton donor	Proton acceptor
3. Lewis	Acceptor of lone pair of electrons	Donor of lone pair of electrons.

- **NaOH is a strong alkali but ClOH is an acid—Explain why ?**

The presence of —OH group in a compound does not mean that the compound will be an alkali. Thus inspite of the presence of —OH group both in NaOH and ClOH, NaOH is an alkali while ClOH is an acid. This is because of the fact that Na being a strong electropositive element, the —OH group is attached to it by electrovalent bond i.e., the bond between oxygen and Na is electrovalent which is nothing but a electrostatic force. Thus when NaOH is treated with water the bond between Na and OH becomes weaker in presence of a polar solvent like water. So NaOH dissociates in its aqueous solution as Na^+ and OH^- ions. Due to the presence of OH^- ions as the only anions in its aqueous solution, it exhibits alkaline property.

In ClOH molecule the oxygen atom of the —OH group is attached to the Cl atom by covalent bond. The chlorine and oxygen both being strong electronegative element, the electron pair used in forming the covalent bond between oxygen and hydrogen atoms is withdrawn towards the oxygen atom and thus the release of H^+ ion from the —OH group of ClOH becomes easy. As a result ClOH dissociates in its aqueous solution as ClO^- and H^+ $ClOH \rightleftharpoons H^+ + ClO^-$ Due to the presence of H^+ ions in the solution it exhibits acid property.

- **Factors upon which the strength of oxyacids depend.**

The strength of an oxyacid depends on—

(i) the electronegativity and the size of the central element which forms the acid.

(ii) the number of non hydroxyl oxygen atoms which are directly joined to the central element by covalent bonds.

(iii) the number of –OH groups present in the acid.

(a) The strength of similar type of oxyacids consisting of the different elements of the same group, decreases due to the decreasing electronegativity and increasing size of the central elements. Thus the order of strengths of such class of acids are shown below—

$$HClO > HBrO > HIO$$

Here the order of electronegativity of the central elements— Cl > Br > I and the order of their size— Cl < Br < I.

(b) The number of non-hydroxyl oxygen atoms joined to the central element of an oxyacid increases the strength of the acid. This is due to the fact that oxygen atoms being very strong electronegative element pull the electron pair from the H atom of the —OH groups towards themselves through the central atom (inductive effect) making easy release of H^+ ions. This is exhibited in the following acids

$$Cl(OH), ClO(OH), ClO_2(OH), ClO_3(OH)$$

The order of strength : $ClO_3(OH) > ClO_2(OH) > ClO(OH) > Cl(OH)$

(c) In the oxyacids of phosphorus such as H_3PO_2, H_3PO_3 and H_3PO_4, the number of additional oxygen atoms joined to the central atom P which increases the strength of the acid by inductive effect is the same i.e., 1 for the three acids, but the number of —OH groups increases from H_3PO_2 to H_3PO_4. As a result the overall inductive effect due to the presence of one non-hydroxyl oxygen atom decreases from H_3PO_2 to H_3PO_4 acid, and so the strength also decreases from H_3PO_2 to H_3PO_4. Thus the order of strength $H_3PO_2 > H_3PO_3 > H_3PO_4$.

Strength of hydracids :

With the increased size of the non metals present in hydracids, the bond strength between the hydrogen atom and the non-metal decreases. Thus the release of H^+ ions from the acids becomes more easy due to the gradual weakening of the bonds.

Thus the order of the strength of halogen acids

$$HI > HBr > HCl > HF$$

Here the order of size of the non-metals joined to H atom is I > Br > Cl > F and the decrease of bond strength is in order $H-F > H-Cl > H-Br > H-I$

Thus the order of strength of H_2O, H_2S, H_2Se is given below—

$$H_2Se > H_2S > H_2O$$

5.8. Salts.

Salts are compounds formed by the partial or complete replacement of the replaceable hydrogen atom or atoms of an acid by a metal or a group of elements behaving as a metal.

Acid	No. of replaceable H-Atom	SALT	
		H–Partially replaced by metal or a group	**H–Completely replaced by metal or group**
HNO_3	1	—	$NaNO_3$, NH_4NO_3
H_2SO_4	2	$NaHSO_4$, NH_4HSO_4	Na_2SO_4, $(NH_4)_2SO_4$
H_3PO_4	3	NaH_2PO_4, Na_2HPO_4	Na_3PO_4, $(NH_4)_3PO_4$

A salt consists of two parts—(i) *basic radical* and (ii) *acid radical*.

Salt	Basic radical	Acid radical
KCl	K^+	Cl^-
$Mg(NO_3)_2$	Mg^{++}	$2NO_3^-$
$Al_2(SO_4)_3$	$2Al^{+++}$	$3SO_4^{--}$

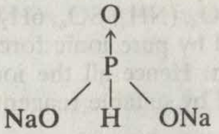
5.9. Classification of Salts.

Salts are usually classified as (i) Normal salt, (ii) Acid salt, (iii) Basic salt, (iv) Double salt and (v) Complex salt.

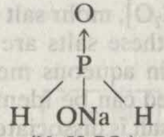
(i) **Normal salt :** *The salt which is produced by the complete removal of the hydrogen atom or atoms of an acid by a metal or a group of elements behaving like a metal is known as normal salt.* Examples—

Acid	Normal salts, produced by the complete removal of H atom			
HCl	NaCl,	KCl,	NH_4Cl,	$MgCl_2$
H_2SO_4	Na_2SO_4,	K_2SO_4,	$(NH_4)_2SO_4$,	$ZnSO_4$
H_3PO_4	Na_3PO_4	K_3PO_4,	$(NH_4)_3PO_4$,	$Mg_3(PO_4)_2$

Monobasic acid always gives normal salts. A normal salt does not contain replaceable hydrogen atom or —OH group. There are some normal salts which may contain hydrogen atom or atoms, but these hydrogen atom(s) being joined to the central atom directly, do not ionise in aqueous medium. Thus Na_2HPO_3 disodium hydrogen phosphite, NaH_2PO_2 sodium hypo phosphite are normal salts.



(Na_2HPO_3)



$(Na\,H_2\,PO_2)$

(ii) **Acid salt :** *The salt which is produced by the partial replacement of the replaceable hydrogen atoms of poly basic acid by a metal or a group of elements behaving as a metal is called acid salt or bi salt.*

Examples—

Acid	*Acid salts*
H_2SO_4	Sodium hydrogen sulphate ($NaHSO_4$) Ammonium bi sulphate [$(NH_4)HSO_4$]
H_2CO_3	Sodium bi carbonate ($NaHCO_3$), Ammonium bi carbonate (NH_4HCO_3) Calcium bi carbonate [$Ca(HCO_3)_2$]
H_3PO_4	Sodium di hydrogen phosphate (NaH_2PO_4) Di sodium hydrogen phosphate (Na_2HPO_4)

Dibasic acids form one type of acid salts.

$$H_2SO_4 + KOH = KHSO_4 + H_2O$$

Tribasic acids form two types of acid salts.

$$H_3PO_4 + KOH = KH_2PO_4 + H_2O$$
$$H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O$$

Acid salts react with strong alkalis to give normal salts.

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O$$

A Soluble acid salt in its aqueous solution gives H^+ ions along with the metallic and acid radical. Such solutions may be acidic or alkaline e.g., an aqueous solution of $NaHCO_3$ is alkaline but that of $(NH_4)HSO_4$ is acidic.

(iii) **Basic salt :** *The salts which are produced by the partial replacement of the hydroxyl groups of a poly acidic base by an acid radical are called basic salts.*

This class of salts are produced by the reaction of an acid with higher proportion of the base than what is required for the formation of a normal salt.

Examples :

$$\begin{array}{lclcll}
\textit{base} & & & & \textit{basic salt} & \\
Pb(OH)_2 & + & HCl & = & Pb(OH)Cl & + \; H_2O \\
Pb(OH)_2 & + & HNO_3 & = & Pb(OH)NO_3 & + \; H_2O \\
2Cu(OH)_2 & + & H_2SO_4 & = & Cu(OH)_2, CuSO_4 & + \; 2H_2O \\
Bi_2O_3 & + & 2HCl & = & 2BiOCl & + \; H_2O
\end{array}$$

Basic salts give OH^- ions in aqueous solution.

$$Pb(OH)NO_3 \rightleftharpoons Pb^{++} + OH^- + NO_3^-$$

Basic salts react with acid to form normal salts.

$$Cu(OH)_2, CuCO_3 + H_2CO_3 = 2CuCO_3 + 2H_2O$$

(iv) **Double salts :** *When two normal salts are mixed in aqueous solution in molecular proportions, and the resulting mixture is allowed to crystallise, the crystals of a single salt separate out which is known as double salt.*

Thus when an equimolecular mixture of K_2SO_4 and $Al_2(SO_4)_3$ solution is allowed to crystallise, crystals of a new single salt separate out which is known as alum $[K_2SO_4, Al_2(SO_4)_3, 24H_2O]$. The other examples of double salts are—chrome alum $[K_2SO_4, Cr_2(SO_4)_3, 24H_2O]$, mohr salt $[FeSO_4, (NH_4)_2SO_4, 6H_2O]$.

The components of these salts are held by pure ionic force, so they undergo complete dissociation in aqueous medium. Hence all the ions, from which the double salt was obtained can be identified by suitable reagents. No new ions are formed when a double salt is dissociated.

$$\begin{array}{lllclclclcl}
FeSO_4 & (NH_4)_2SO_4 & 6H_2O & = & Fe^{++} & + & 2NH_4^+ & + & 2SO_4'' & + & 6H_2O \\
KCl & MgCl_2 & 6H_2O & = & K^+ & + & Mg^{++} & + & 3Cl^- & + & 6H_2O
\end{array}$$

(v) **Complex salt :** In some cases when the solutions of two normal salts are mixed together and the mixed solution is allowed to crystallise, the crystals of a new salt separate out. The salt thus produced is completely different from those of the individual normal salt. In its aqueous solution it does not give the ions of the original salts but gives complex and simple ions. Salt of this type is known as complex salt. Thus when an aqueous solution of KCN is added to dirty green precipitate of $Fe(CN)_2$, the later dissolves. The solution, on being crystallised forms potassium ferrocyanide $K_4[Fe(CN)_6]$. The later does not respond to the test of Fe^{++} or CN^- in aqueous medium but forms a new entity $[Fe(CN)_6]^{4-}$ (a complex ion).

$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]$$
$$K_4[Fe(CN)_6] = 4K^+ + [Fe(CN)_6]^{4-}$$

Ionisation of some complex salts are given here—

$$K_3[Fe(CN)_6] \rightleftharpoons 3K^+ + [Fe(CN)_6]^{3-}$$

Pot. ferricyanide

$$K_2SiF_6 \rightleftharpoons 2K^+ + [SiF_6]^{2-}$$

Pot. silico fluoride

$$Na_3[Co(NO_2)_6] \rightleftharpoons 3Na^+ + [Co(NO_2)_6]^{3-}$$

Sodium cobaltinitrite

$$\underset{\text{Cupro ammonium sulphate}}{[Cu(NH_3)_4]SO_4} \rightleftharpoons [Cu(NH_3)_4]^{++} + SO_4^{--}$$

The groups attached to the central metal ion are known as ligands.

Examples of ligands : CN^-, F^-, NO_2^-, SCN^-, NH_3, H_2O etc. Complex salts were first studied by Alfred Werner who called them *"co-ordinate compounds"*.

An apparently insoluble substance passes into solution through the formation of complex ions. The method is often used in analytical chemistry. Some examples are :—

(a) *Iodine is sparingly soluble in water but it dissolves in solution containing I^- ion e.g., KI. This is due to the formation of complex ion (I_3^-) in aqueous medium.*

$$I_2 + I^- \rightleftharpoons I_3^- \text{ i.e. } KI + I_2 = KI_3$$

(b) When KI solution is added to an aqueous solution of $HgCl_2$, at first a deep red precipitate of HgI_2 is formed. On adding excess KI, the precipitate dissolves forming a colourless solution forming $K_2[HgI_4]$. An alkaline solution of the latter is known as *Nessler's reagent.*

$$2KI + HgCl_2 = HgI_2 + 2KCl$$
$$HgI_2 + 2KI = K_2[HgI_4]$$

5.10. Oxides.

Oxygen being an active element combines with all elements—metals and non-metals, directly or indirectly to form compounds. Such binary compounds are known as oxides.

An oxide is defined as the binary compound formed by the union of oxygen and another element.

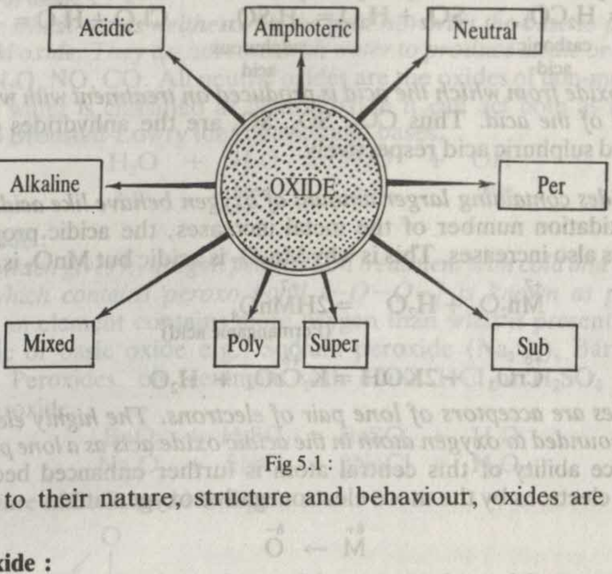


Fig 5.1 :

According to their nature, structure and behaviour, oxides are classified as follows :—

(i) Basic Oxide :

Basic oxides are generally the oxides of metals which react with acids to produce salts and water only, e.g., sodium oxide (Na_2O), calcium oxide (CaO), cupric oxide (CuO), ferric oxide (Fe_2O_3) etc.

$$\begin{array}{lclcl} \text{Basic oxide} + & \text{acid} & \rightarrow & \text{salt} & + \text{ water} \\ CuO & + 2HCl & = & CuCl_2 & + H_2O \\ MgO & + H_2SO_4 & = & MgSO_4 & + H_2O \end{array}$$

Basic oxide if soluble in water, produces soluble base or alkali. This solution turns red litmus blue and gives OH^- ions as anion.

$$4Na + O_2 = 2Na_2O \ ; \quad Na_2O + H_2O = 2NaOH$$
$$NaOH \rightleftharpoons Na^+ + OH^-$$

The basic oxide contains oxygen atoms with electron pairs available for bonding. When oxygen is linked with a strong electropositive element, the bond between them becomes polar and oxygen atom acquires a large negative charge. As the density of this negative charge increases, the ability of oxygen for donating the lone pair of electrons also increases and thus the basic character of the basic oxide increases. *As Cs is more electropositive than Li, CsO_2 is more basic than LiO_2. For the same reason Bi_2O_3 is more basic than P_2O_3.*

Soluble basic oxides give OH^- ions in aqueous solution as O—H bond is less polar than the bond between oxygen and the metal in an oxide. The strong polar bond between the metal and oxygen becomes weaker in a polar solvent like water. This is because of the fact that the difference in electronegativities of the central element (say, Mg) and oxygen is much greater than that of oxygen and hydrogen.

$$H{-}O{-}Mg{-}O{-}H + xH_2O \rightleftharpoons [Mg(H_2O)x]^{++} + 2OH^-$$

Hence MgO is a basic oxide.

(2) **Acidic oxide :**

The oxides of non-metals which react with bases to produce salt and water are known as acidic oxides. Such class of oxides if soluble in water forms acids, e.g., SO_2, CO_2, P_2O_5, SiO_2, B_2O_3 etc.

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O, \qquad SO_3 + Na_2O = Na_2SO_4$$

$$\underset{\substack{\text{carbonic}\\ \text{acid}}}{CO_2 + H_2O = H_2CO_3}, \quad \underset{\substack{\text{sulphurous}\\ \text{acid}}}{SO_2 + H_2O = H_2SO_3}, \quad \underset{\substack{\text{hypochlorous}\\ \text{acid}}}{Cl_2O + H_2O = 2HOCl}$$

The acidic oxide from which the acid is produced on treatment with water is called the anhydride of the acid. Thus CO_2, SO_2, SO_3 are the anhydrides of carbonic, sulphurous and sulphuric acid respectively.

Metallic oxides containing larger amount of oxygen behave like acidic oxides. In fact as the oxidation number of the metal increases, the acidic property of the metallic oxides also increases. This is why Mn_2O_7 is acidic but MnO_2 is basic.

$$\overset{+7}{Mn_2}O_7 + H_2O = 2H\overset{+7}{Mn}O_4$$
(Permanganic acid)

$$\overset{+6}{Cr}O_3 + 2KOH = K_2\overset{+6}{Cr}O_4 + H_2O$$

Acidic oxides are acceptors of lone pair of electrons. The highly electronegative central atom bounded to oxygen atom in the acidic oxide acts as a lone pair acceptor. The acceptance ability of this central atom is further enhanced because of the withdrawal of electrons by the more electronegative oxygen atom.

$$\overset{\delta+}{M} \rightarrow \overset{\delta-}{O}$$

Sometime atom of low electronegativity such as Mn or Cr becomes highly electronegative and thus acquires the electron acceptance ability, when a large number of oxygen atoms is attached to it. The electron acceptance ability of the central element of an acidic oxide is enhanced because the oxygen atom pulls the electron pair towards itself as shown above. SO_3 is more acidic than SO_2 because SO_3 contains more oxygen atoms which increases the electro-negativity of S atom in SO_3 and so S atom becomes better electron acceptor. Thus, we can frame a rule—'*The acidic character of an oxide increases with the increase of the number of oxygen atoms attached to the central atom.*'

Thus, MnO is basic, Mn_2O_3 is amphoteric and Mn_2O_7 is strongly acidic.

(3) **Amphoteric oxide :**

The oxide which acts both as basic and acidic oxide is known as amphoteric oxide. This class of oxide reacts with strong acids as well as strong alkalis separately to yield salts and water e.g., ZnO, SnO, PbO, Al_2O_3 etc.

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$
$$ZnO + 2NaOH = Na_2ZnO_2 + H_2O$$

If the partial negative charge on the oxygen atom of an oxide is in between that of a typical acidic oxide and a basic oxide, it will exhibit amphoteric behaviour.

It exhibits the basic character when its bonded oxygen atom acts as donor to the central atom of an acidic oxide which acts as acceptor.

Basic behaviour : $Zn - O\!: \rightarrow SO_3 = ZnSO_4$

It exhibits the acidic character when its central atom acts as acceptor when comes in contact with the bonded oxygen atom having high negative charge of a basic oxide.

Acidic behaviour : $CaO\!: \rightarrow ZnO = CaZnO_2$

In aqueous medium amphoteric oxide may give rise to both $(H_3O)^+$ and OH^- depending on the nature of reactants. If the difference of electronegativity between $O - H$ and $M - O$ is comparable then there is equal chance of release of $(H_3O)^+$ or OH^- in aqueous medium. Hence is the amphoteric behaviour.

(4) **Neutral oxide :**

The oxide which reacts neither with the acid nor with the base to produce salt is called neutral oxide. They do not react with water to produce acidic or basic solution e.g., H_2O, N_2O, NO, CO. All neutral oxides are the oxides of non-metals.

Although water is classified as neutral oxide it can act both as acid and base according to Bronsted-Lowry idea of acids and bases.

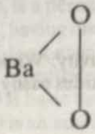
$$\underset{acid_1}{H_2O} + \underset{base_2}{H_2O} \rightleftharpoons \underset{acid_2}{H_3O^+} + \underset{base_1}{OH^-}$$

(5) **Peroxide :**

An oxide which gives hydrogen peroxide on treatment with cold and dilute mineral acids and which contains peroxo bond [−O−O−] is known as peroxide. The peroxide of an element contains more oxygen than what is present in its highest typical acidic or basic oxide e.g., Sodium peroxide (Na_2O_2), Barium peroxide (BaO_2) etc. Peroxides, on treatment with dilute HCl or H_2SO_4 give salt and hydrogen peroxide.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$
$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2$$

The structure of BaO_2 and Na_2O_2 are :—



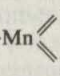
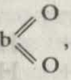
and Na—O—O—Na

Peroxides may be looked upon as salts of the weak dibasic acid H_2O_2. Hence they are hydrolysed in solution.

Oxygen is present in peroxide as peroxide ion $[O-O]^{--}$

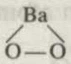
- **Explain why BaO_2 is called peroxide but PbO_2 or MnO_2 is known as dioxide.**

Although the peroxide of an element contains larger proportion of oxygen than what is present in its basic oxides, it is not correct to say that an oxide with higher percentage of O_2 is a peroxide e.g., MnO_2, PbO_2 contain more oxygen than what is present in their normal oxides namely MnO and PbO, yet they are not peroxides. This is because of the fact that (i) these oxides do not yield H_2O_2 on being treated with cold dilute mineral acids. (ii) They do not contain any peroxo link (–O–O–) in their molecules but the oxygen atoms are attached to the metals covalently with the formation of double bonds e.g.,

$MnO_2 \rightarrow$ , $PbO_2 \rightarrow$, , (iii) They produce Cl_2 and O_2 when treated with hot concentrated HCl and H_2SO_4 respectively.

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$
$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + O_2 + 2H_2O$$

Consequently these oxides are generally called dioxides and not peroxides.

But BaO_2 is peroxide as it conforms to the properties of peroxide. BaO_2 on being treated with cold and dilute H_2SO_4 yields hydrogen peroxide. $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$. BaO_2 contains peroxo bond in its molecule. 

(6) **Mixed oxides :**

The oxide which is formed by the union of two oxides of same metal in different valency state, is called a mixed oxide. On being reacted with acids they yield mixture of salts corresponding to metal in different valency state e.g., *Ferrosoferric oxide* (Fe_3O_4), (*A mixture of FeO and Fe_2O_3*). Similarly, *red lead* Pb_3O_4 ($2PbO + PbO_2$), Mn_3O_4 ($2MnO + MnO_2$) etc. are examples of mixed oxides.

$$Fe_3O_4 + 8HCl = 2FeCl_3 + FeCl_2 + 4H_2O$$
$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O$$

(7) **Polyoxide :**

An oxide which contains more oxygen than either the acidic or basic oxide but does not produce H_2O_2 on being treated with dilute mineral acids is called Poly oxides e.g., Mn_2O_7, PbO_2, MnO_2 etc.

(8) **Suboxide :**

There are some oxides in which the element combined with oxygen, is in unusually low oxidation state. *Carbon suboxide* (C_3O_2) is an example of this class. However, suboxides are normal oxides with respect to oxygen. The structure of C_3O_2 is $O=C=C=C=O$

(9) **Superoxide :**

Latter members of alkali metals e.g., Cs, Rb, K form a type of oxide which contains a lattice of calcium carbide type in which the anionic species is O_2^- ion. The anion has the structure $\left[\,:\underset{\bullet\bullet}{O}\overset{\bullet\bullet\bullet}{-}\underset{\bullet\bullet}{O}:\,\right]^-$ involving a single bond and a 3-electron bond between two oxygen atoms. All *superoxides are paramagnetic and coloured.* Superoxide ion contains 1 unpaired electron e.g., KO_2, NaO_2, CsO_2, $Ca(O_2)_2$

- **Superoxides are strong oxidising agent—Explain.**

Superoxides differ from peroxides with respect to structure and reactivity. While peroxides liberate H_2O_2 with cold dilute acids, superoxides liberate oxygen. As the super oxides easily liberate O_2 they are strong oxidising agents.

$$4KO_2 + 2H_2SO_4 = 2K_2SO_4 + 2H_2O + 3O_2$$

with ice cold water KO_2 forms O_2 in addition to H_2O_2

$$2KO_2 + 2H_2O = 2KOH + H_2O_2 + O_2$$

• Exercises •

1. Define acid in the light of electrotytic dissociation. In what different ways are the acids classified ?

2. State briefly Arrhenius theory of acids and bases. Mention the limitations of this theory.

3. State briefly the modern concept of acids and bases according to (i) Bronsted-Lowry, (ii) Lewis-State the limitations of each concept.

4. What is an alkali ? Distinguish between alkali and base.

5. Explain the terms with examples—(i) Strong acid and weak acid, (ii) Strong base and weak base, (iii) basicity of acid and acidity of base.

6. Mention the basicity of the following acids—CH_3COOH, $HCOOH$, H_3PO_2, H_3PO_3, H_3PO_4, H_2SO_4 *[H.S. 90]*

7. What is salt ? Distinguish between acid salt and basic salt.

8. Define with examples—normal salt acid salt, basic salt, double salt and complex salt.

9. State with reasons the types of the following salts—$NaHCO_3$, $Cu(OH)_2$, $CuSO_4$; $BiOCl$; NH_4Cl ; $KClO_4$; $Ca(HCO_3)_2$; $NaOCl$, Na_2HPO_3 ; Na_2SO_4 ; K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$.

10. Identify the acids and bases according to Bronsted-Lowry concept from the following— H_3O^+, H_2O, NH_4^+, HCO_3^-, CH_3COO^-, $AlCl_3$

11. Identify Lewis acids and bases from the following :

$AlCl_3$, NH_3, BF_3, Cu^{2+}, H^+, OH^-

12. Arrange the following acids in order of increasing acidity and explain your choice— *[I.I.T. '86]*

(a) $HClO_4$, $HClO_3$, $HClO_2$ and $HOCl$
(b) $HOCl$, $HOBr$, HOI
(c) $CH_3\,COOH$, $CH_2Cl\,COOH$, $CH_2\,FCOOH$

13. Explain the terms conjugate acids and conjugate bases. Write the equations for (i) ionisation of HCOOH in aqueous solution, and label the conjugate acid base pair.

14. Define and classify oxides. State with reasons what is the type of the following oxides.

Al_2O_3, ZnO, NO, BaO_2, PbO_2, Fe_3O_4, SO_3, CO, H_2O

15. Give the conjugate bases of (i) H_3O^+, (ii) HNO_3, (iii) HI, (iv) NH_4^+, (v) HCO_3^-, (vi) OH^- *[Roorke Eng., '87]*

16. Distinguish between (i) Acid salt and normal salt, (ii) Acidic oxide and basic oxide *[H.S. 81]*, (iii) Amphoteric oxide and neutral oxide *[H.S. 80]*

17. Write short notes on : (i) Acidic oxide *[H.S. 87]* (ii) Basic oxide *[H.S. 81]*, (iii) Mixed oxide, (iv) Amphoteric oxide *[H.S. 83]*, (v) Peroxide *[H.S. 90]*

18. Write down the conjugate acid and conjugate base of NH_3 and HCO_3^- *[Roorke Eng. '87]*

19. Explain—

(i) Ortho phosphoric acid behaves as a dibasic acid. *[H.S. 91]*
(ii) In aqueous solution H_3PO_4 is tribasic but H_3PO_3 is dibasic. *[J.E. 89]*
(iii) H_3PO_4, H_3PO_2 and H_3PO_3—all of them contains 3 hydrogen atoms but the basicity of the three acids are different. *[I.I.T. 87]*
(iv) HCl and HNO_3 always form normal salts.
(v) NaOH is an alkali but ClOH is acidic.
(vi) Anhydrous HCl can not turn blue litmus red.
(vii) CH_3OH is not an oxyacid.
(viii) NH_3 does not contain oxygen yet it is alkaline.
(ix) $AlCl_3$ is a Lewis acid.
(x) Dilute H_2SO_4 is a stronger acid than conc. H_2SO_4.
(xi) SiO_2 is an acidic oxide. *[H.S. 80]*
(xii) All acids contain hydrogen but all compounds containing hydrogen are not acids .
(xiii) The basicity of an acid does not depend upon the number of hydrogen atoms present in it.
(xiv) CO is a neutral oxide.
(xv) MgO is a basic oxide but Cl_2O_7 is an acidic oxide.
(xvi) BaO_2 is a peroxide but MnO_2 or PbO_2 is a dioxide. *[H.S. 89] [JE 87]*
(xvii) NH_3 having one lone pair is a base while N_2 molecule containing 2 lone pairs has no basic property.
(xviii) BF_3 is a Lewis acid but pyridine is a Lewis base.
(xix) NO_2 is neutral oxide but N_2O_5 is an acidic oxide.
(xx) MnO is basic but Mn_2O_7 is acidic oxide. *[I.S.C. 89]*
(xxi) ZnO is an amphoteric oxide. *[H.S. 82]*

(xxii) Cl_2O_7 is more acidic than Cl_2O_5.
(xxiii) HI is the strongest of the halogen acids.
(xxiv) H_2SO_4 is stronger than H_2SO_3.
(xxv) NH_3 is more basic than PH_3. [*H.S. 91*]
(xxvi) A bare proton does not exist in water.
(xxvii) NH_3 is Lewis base and water is amphiprotic.
(xxviii) H_2S is weaker than H_2Se.
(xxix) Some salts contain replaceable hydrogen but others do not.
(xxx) Fe_2O_3 is a basic oxide while Al_2O_3 is an amphoteric.
(xxxi) All alkalis are bases but all bases are not alkalis.
(xxxii) All acids contain hydrogen, but all hydrogen containing compounds are not acids.
(xxxiii) NaH_2PO_2 is a normal salt.
(xxxiv) CsO_2 is more basic than LiO_2.
(xxxv) Super oxides are strong oxidising agents.

20. (a) How can you distinguish between Na_2CO_3 and $NaHCO_3$ with the help of an indicator ? [*Jt. Ent. '90*]

(b) Pure liquid hydrogen chloride and pure water are both bad conductors of electricity, but an aqueous solution of hydrogen chloric acid is an electrolyte—Explain why giving reasons. [*Jt. Ent. '86*]

21. (a) Why anhydrous hydrogen chloride does not turn blue litmus red ?

(b) The basicity of H_3PO_2 is one. What idea can you have about the structure of H_3PO_2 from the above information ?

22. Both H_2SO_4 and NaOH contain OH group, but the former is an acid while the later is an alkali—how would you explain this ?

23. Which os the following pairs can not remain together in aqueous solution ? (i) $NaHCO_3$ and NaOH ; (ii) Na_2CO_3 and $NaHCO_3$; (iii) Na_2CO_3 and NaOH : (iv) $NaHCO_3$ and NaCl.

24. What are the anhydrides of (i) H_2SO_4 ; (ii) HNO_3 ; (iii) NaOH ; (iv) H_3PO_4 ; (v) $Cr(OH)_3$; (vi) $HClO_4$

25. Give examples of (i) Solid acidic oxides, (ii) Super oxide, (iii) Compound oxide, (iv) Sub oxide.

ACIDIMETRY AND ALKALIMETRY

6

Introduction.

Qualitative detection and quantitative estimation of a substance are the two most important objectives of analytical chemistry. Acidimetry and alkalimetry i.e., determination of strength of acid and alkali in solution comes under the perview of analytical chemistry. In general this is referred to volumetric analysis. We know that 1 gram equivalent of an acid neutralises 1 gram equivalent of alkali to yield salt and water.

$$\textbf{Acid} + \textbf{Alkali} = \textbf{Salt} + \textbf{Water}$$

Based on this principle the strength of an unknown acid is determined with the help of a known strength of an alkali or vice versa.

6.1. Equivalent Weight of Acid, Base and Salt.

[A] Equivalent weight of an acid :

The equivalent weight of an acid is defined as the number of parts by weight of the acid which contains 1·008 parts (very nearly 1 part) by weight of replaceable hydrogen.

Examples : (i) The molecular weight of H_2SO_4 is 98. It contains 2 parts by weight of replaceable hydrogen. Hence the equivalent weight of $H_2SO_4 = \frac{98}{2} = 49$.

(ii) The molecular weight of HCl is 36·5. It contains 1 part by weight of replaceable hydrogen. Hence the equivalent weight of $HCl = \frac{36\cdot5}{1} = 36\cdot5$.

Since the number of replaceable hydrogen atoms denotes the basicity of an acid, we can express the equivalent weight of an acid as follows—

$$\text{Equivalent weight of an acid} = \frac{\text{Molecular weight of the acid}}{\text{Basicity of the acid}}$$

Mol. wt. of $H_2SO_4 = 98$. Its basicity$=2$

$\therefore$ Equivalent weight of $H_2SO_4 = \frac{98}{2} = 49$

Similarly Mol. wt. of $HNO_3 = 63$. Its basicity$=1$

$\therefore$ Equivalent weight of $HNO_3 = \frac{63}{1} = 63$

Equivalent weight of $H_3PO_4 = \frac{92}{3} = 32\cdot67$. (assuming H_3PO_4 as tribasic acid)

Alternatively, the equivalent weight of an acid is defined as that quantity of acid by weight which gives rise to 1 part by weight of H^+ ion in its aqueous solution.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

H_2SO_4, on being ionised gives rise to 2 parts by weight of H^+ ion in its aqueous solution.

Hence, Eq. wt. of $H_2SO_4 = \frac{98}{2} = 49$.

- **Gram equivalent weight of an acid :** When the equivalent weight of an acid is expressed in gram, it is called the gram equivalent weight or simply gram equivalent of acid.

Thus, *gram equivalent weight of an acid is defined as the quantity of the acid in gram, which contains 1·008 gram of replaceable hydrogen.*

$$\text{Gram equivalent weight of acid} = \frac{\text{Gram molecular weight of the acid}}{\text{Basicity of the acid}}$$

Thus the equivalent weight of $H_2SO_4 = \frac{98}{2} = 49$.

$\therefore$ 49 g of $H_2SO_4 = 1$ gram equivalent of H_2SO_4.

[B] Equivalent weight of a base : *It is defined as the number of parts by weight of the base or alkali, which neutralises one equivalent weight of an acid.*

Examples : (i) In finding out the equivalent weight of a base, its reaction with an acid is to be considered.

The equivalent weight of $H_2SO_4 = 49$.

Now considering the reaction of NaOH with H_2SO_4

$$\underset{\substack{2\times40\\ \text{parts by wt.}}}{2NaOH} + \underset{\substack{98\text{ parts}\\ \text{by wt.}}}{H_2SO_4} = Na_2SO_4 + 2H_2O$$

From the reaction it is found that 40 parts by weight of NaOH neutralise 49 parts by weight. (one equivalent weight) of H_2SO_4. Hence the equivalent weight of NaOH=40.

(ii) Considering the reaction of MgO with H_2SO_4,

$$\underset{\substack{40\text{ parts}\\ \text{by wt.}}}{MgO} + \underset{\substack{98\text{ parts}\\ \text{by wt.}}}{H_2SO_4} = MgSO_4 + H_2O$$

It is found that 49 parts by weight of H_2SO_4 is neutralised by 20 parts by weight of MgO. Hence, the equivalent weight of MgO=20.

$$\text{Thus, the equivalent weight of a base} = \frac{\text{Molecular weight of the base}}{\text{Acidity of the base}}$$

e.g., Equivalent weight of CaO $= \frac{56}{2} = 28$

Equivalent weight of $Fe_2O_3 = \frac{160}{2\times3} = 26{\cdot}6$.

Equivalent weight of $Ca(OH)_2 = \frac{74}{2} = 37$.

[C] Equivalent weight of a salt : *The equivalent weight of a salt is defined as the number of parts by weight of the salt which contains one equivalent of active cation or anion present in the salt.*

Thus, the equivalent weight of salt=

$$\frac{\text{Molecular weight of the salt.}}{\text{Number of cations or anions} \times \text{valency of the cation or anion}}$$

Equivalent wt. of $Al_2(SO_4)_3 = \frac{342}{3\times2} = 57$

Equivalent wt. of $(NH_4)_2SO_4 = \frac{96}{1\times2} = 48$

Equivalent wt. of $CuSO_4, 5H_2O = \frac{249{\cdot}5}{1\times2} = 124{\cdot}75$

- **Equivalent weight of carbonates and bi-carbonates :** Both carbonates and bi-carbonates react with acid to form salt and H_2O in addition to CO_2. Hence their gram equivalents are their weight in gram that exactly neutralise one gram equivalent weight of an acid.

$$\underset{106\,g}{Na_2CO_3} + \underset{2\times 36\cdot 5\,g}{2HCl} = 2NaCl + CO_2 + H_2O$$

∴ The gram equivalent of $Na_2CO_3 = \frac{106}{2} = 53$ g

• **Equivalent weight of oxidising agents :** *The equivalent weight of an oxidising agent is defined as the number of parts by weight of it which contains 8 parts by weight of available oxygen.*

Examples : (i) $K_2Cr_2O_7$ decomposes as, $\underset{294}{K_2Cr_2O_7} = K_2O + Cr_2O_3 + \underset{3\times 16}{3O}$

Here 48 parts by wt. of O_2 are available from 294 parts by wt. of $K_2Cr_2O_7$

∵ 8 ” ” ” ” ” ” ” ” $\frac{294\times 8}{48} = 49$ ” ” ” ”

∴ the equivalent weight of $K_2Cr_2O_7 = 49$.

(ii) $KMnO_4$ decomposes as $\underset{2\times 158}{2KMnO_4} = K_2O + 2MnO + \underset{5\times 16}{5O}$

Here 80 parts by wt. of O_2 is available from 2×158 parts by wt. of $KMnO_4$

∴ 8 ” ” ” ” ” ” ” ” $\frac{2\times 158\times 8}{80} = 31\cdot 6$ ” ”

∴ the equivalent weight of $KMnO_4 = 31\cdot 6$.

• **Equivalent weight of a reducing agent :** *The equivalent weight of a reducing agent is the number of parts by weight of it, which reacts with one equivalent weight of an oxidising agent.*

Examples : $\underset{2\times 152}{2FeSO_4} + \underset{98}{H_2SO_4} + O = Fe_2(SO_4)_3 + H_2O$

Here, the equivalent of H_2SO_4 (oxidising agent) = 49.

∵ 98 parts by wt. of H_2SO_4 reacts with 2×152 parts by wt. of $FeSO_4$

∴ 49 ” ” ” ” ” ” ” ” $\frac{2\times 152\times 49}{98} = 152$ ” ” ” ”

∴ the equivalent weight of $FeSO_4$ (reducing agent) = 152.

6.2. Concentration of a solution.

The concentration of a solution indicates the relative amounts of the solute and the solvent present in the solution. The concentration of a solution is expressed in various ways e.g., **normality, molarity, molality, formality, gram per litre** and **percent strength.**

(1) Normality :

Normality of a solution is the number of gram equivalents of the solute present per litre (1000 ml) of the solution.

$$\therefore \text{Normality} = \frac{\text{Weight of the solute in gram present in 1 litre of the soln.}}{\text{Equivalent weight of the solute}}$$

Let *m* g of the solute is dissolved in a solvent to make *l* litres of the solution. Let *E* be the equivalent weight of the solute.

∴ The number of gram-equivalent of the solute $= \frac{m}{E}$

Thus *l* litre of the soln. contain $\frac{m}{E}$ gram-equivalent of solute.

∴ 1 litre ” ” ” ” $\frac{m}{l\times E}$ ” ” ”

Hence, the normality of the soln. $= \frac{m}{l \times E}$ or, $\frac{m/l}{E}$

Now m/l=weight in gram of the solute per litre (1000 ml) of the solution.

Hence Normality= $\frac{\text{Weight in gram of solute per litre of the solution}}{\text{Gram-equivalent of the solute}}$

Thus, if 1 litre of the solution contains 1 gram-equivalent of the solute, the solution is 1 normal. Similarly if 1 litre of the solution contains 2 gram-equivalents of the solute it is 2 normal and so on. Hence if 1 litre of the solution contains *n* gram-equivalent of the solute the normality of the solution is *n* normal.

- **Normal solution :** *A normal solution is defined as a solution, 1 litre of which contains 1 gram-equivalent weight of the solute.* It is represented by the symbol N.

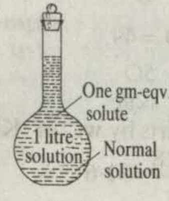


Fig 6.1 :

Gram-equivalent of NaOH is 40 g. Thus when 1 litre solution of NaOH contains 40 g of NaOH the resulting solution is 1(N) NaOH.

Example : When 80 g (or 2 gram-eq.) of NaOH are dissolved in 1 litre solution, the normality is 2. Similarly when 200 g, (5 gram-eq.), 20 g (0·5 gram-eq.) or 4 g (0·1 gram-eq.) of NaOH are present per 1000 ml solution or 1 litre solution the resulting solutions are 2(N), 5(N), 0·5(N) and 0·1(N) respectively.

In this connection remember that if 1 gram-eq. of a solute is dissolved in 1 litre or 1000 ml water, the resulting solution is not 1(N). The total volume 1 litre will include both solute and solvent.

Sometimes 1 litre of solution contains multiples or functions of gram-eq. of solute. Thus if $\frac{1}{10}$th gram-eq. of a solute is present per litre of the solution, the resulting solution is deci-normal, and is represented by $\frac{N}{10}$ or 0·1 N. If 1000 ml of the solution contains 2 gram-equivalents of the solute, the resulting solution is 2N and so on. The following table illustrates the way of representing the normality of the solution when multiples or fractions of gram-equivalents of the solute is present in 1 litre of the solution.

Amount of solute per litre of the solution	Name and symbol of the solution	Strength in Normality
1 gram-equivalent	Normal solution (N)	1
0.5 ,,	Seminormal ,, 0.5(N)	1/2=0·5
0.01 ,,	Centinormal ,, 0·01(N)	0·01
2 ,,	Two normal ,, 2(N)	2
0·6 ,,	Six decinormal ,, 0·6(N)	0·6
x ,,	*x* normal ,, *x*(N)	*x*
0·3 ,,	Three decinormal ,, 0·3(N)	0·3
0·1 ,,	decinormal ,, 0·1(N)	0·1

- **Normality Factor :**

Sometimes it is very difficult, though not impossible to weigh out *exactly* the gram-equivalent of a solute. What we weigh in chemical balance is some multiples or fractions of gram-equivalent of a solute. Thus to prepare 1(N) H_2SO_4, we are to weigh exactly 49 g of H_2SO_4. If instead of 49 g, we weight 50 g of H_2SO_4 and dissolve in water to make 1 litre, the strength of the solution will not be exactly (N), but it will be a little stronger than (N) H_2SO_4. If we weigh 48 g of H_2SO_4 and make 1 litre solution out it, the resulting solution will be a little weaker than 1(N) H_2SO_4. The idea of this change of strength from exactly a normal solution is given by a factor that denotes a number (more or less than 1) which is the ratio of the weight of the solute taken by actual weighing, to the weight of the solute to be taken theoretically.

Hence, Normality factor=

$$\frac{\text{Weight in gram of the solute actually taken.}}{\text{Weight in gram of the solute to be taken to make the solution of given strength}}$$

Thus normality factor is defined as the ratio of the weights of the solute actually dissolved in a definite volume of solution, to its exact required gram-equivalent to prepare a solution of given strength.

Thus when 50 g of H_2SO_4 is present per 1000 ml of the solution, the weight of H_2SO_4 is $\frac{50}{49}$ parts of the equivalent weight of H_2SO_4 (49 is the gram-equivalent of H_2SO_4).

This $\frac{50}{49}$ or 1·0204 is called the normality factor of that H_2SO_4 and the strength of H_2SO_4 is represented as 1·0204(N). The symbol of normality is factor is *f* or here $f=1\cdot0204$. Similarly in the latter case i.e., when 48 g of H_2SO_4 is present per 1000 ml of the solution the normality factor is $\frac{48}{49}=0\cdot97$ and solution is 0·97(N) H_2SO_4.

(2) **Gram of solute per litre :**

This is the number of gram of solute in 1 litre of the solution. We have already defined normality of a solution as follows :—

$$\text{Normality} = \frac{\text{Weight in gram of the solute per litre of the solution}}{\text{Gram-equivalent of the solute}}$$

or, Weight in gram of the solute per litre of the solution

=Normality of the solution × Gram-eq. of the solute

Thus, (N) H_2SO_4 means 49 g of H_2SO_4 is present in 1 litre of the solution.

Again, 0·2 (N) H_2SO_4 means $0\cdot2 \times 49 = 9\cdot8$ g of H_2SO_4 in 1 litre of solution.

Similarly, $\frac{N}{10}$ HCl denotes presence of 3·65 g of HCl in 1 litre of solution.

The following table will indicate the weight of solute per 1 litre of the solution.

Solute	**Gram-eq. of solute**	**Volume of the solution**	**Strength of the solution**	**Weight in gram in 1 litre of the solution**
HCl (M=36·5)	36·5 g	1000 ml or 1 litre	3N	$3 \times 36\cdot5 = 109\cdot5$ g
			1N	$1 \times 36\cdot5 = 36\cdot5$ "
			0·5N	$0\cdot5 \times 36\cdot5 = 18\cdot25$ "
			0·1N	$0\cdot1 \times 36\cdot5 = 3\cdot65$ "
			N/3	$1/3 \times 36\cdot5 = 12\cdot166$ "
H_2SO_4 (M=98)	49 g	"	3N	$3 \times 49 = 147$ g
			1N	$1 \times 49 = 49$ "
			0·5N	$0\cdot5 \times 49 = 24\cdot5$ "
			0·1N	$0\cdot1 \times 49 = 4\cdot9$ "
			N/3	$1/3 \times 49 = 16\cdot33$ "

Solute	Gram-eq. of solute	Volume of the solution	Strength of the solution	Weight in gram in 1 litre of the solution
Na_2CO_3 (M=106)	53 g	I litre, or 1000 ml	3N	$3 \times 53 = 159$ g
			1N	$1 \times 53 = 53$ ”
			0·5N	$0{\cdot}5 \times 53 = 26{\cdot}5$ ”
			0·1N	$0{\cdot}1 \times 53 = 5{\cdot}3$ ”
			N/3	$1/3 \times 53 = 17{\cdot}66$ ”
NaOH (M=40)	40 g	”	3N	$3 \times 40 = 120$ g
			1N	$1 \times 40 = 40$ ”
			0·5N	$0{\cdot}5 \times 40 = 20$ ”
			0·1N	$0{\cdot}1 \times 40 = 4{\cdot}0$ ”
			N/3	$1/3 \times 40 = 13{\cdot}33$ ”

(3) **Molarity (M) :** *The molarity of a solution is the number of gram moles of the solute present in one litre of the solution.* Thus if 1 mole of solute is dissolved in 1 litre of solution, the solution is said to be 1M (M = symbol of molarity). Similarly if $\frac{1}{10}$th of a mole of a solute is dissolved in 1 litre of solution, it is said to be decimolar $\left(\frac{M}{10}\right)$.

Thus, 1 (M) H_2SO_4 solution contains 98 g of H_2SO_4 per litre of solution. If $98 \times 3 = 294$ g of H_2SO_4 are present in 1000 ml of the solution, it is said to be 3 (M) H_2SO_4.

Let a g of solute of molecular weight m be dissolved in V litres of solution.

$\therefore$ Number of moles of solute $= \dfrac{a}{m}$

Thus,

V litre solution contain $\dfrac{a}{m}$ moles of solute

or, 1 litre solution contains $\dfrac{a}{m \times V}$ moles of solute

or, the molarity of the solution $(M) = \dfrac{a}{m \times V} = \dfrac{a/V}{m}$

or, Molarity of the solution $(M) = \dfrac{\text{Weight of the solute in gram per litre}}{\text{Gram-Molecular weight of the solute}}$

$\therefore$ Weight of the solute in gram per litre

= Molarity of the solution × Gram-Mol. weight of the solute

(4) **Molar solution :**

A molar solution is defined as a solution, 1 litre of which contains 1 gram-mole or 1 mole of the solute.

When **gram-mole** and **gram-eq.** of a solute are the same, the normality and molarity of the solution are also same. The gram-eq. and gram-mole of HCl is 36·5. Hence normal and molar solution of HCl are identical. But if gram-eq. and gram-mole of a solute are different, normality and molarity of the solution will be different. Thus 98 g = 1 gram-mole of H_2SO_4, and 49 g = 1 gram-eq. of H_2SO_4. Hence :—

$\therefore$ 1(M) H_2SO_4 = 2(N) H_2SO_4

or, 1 (N) H_2SO_4 = 0·5 (M) H_2SO_4

Thus in the case of mono acidic bases and mono basic acids, the equivalent and molecular weights are the same. In these cases Molarity and Normality are the same.

In general, if equivalent weight $=1/n\times$ molecular weight.

Normality of the solution $=n\times$ molarity.

The following table indicates the amount of solute, symbol and molarity of some solutions.

Amount of solute in 1 litre of solution	Name and Symbol of the solution	Molarity
1·0 gram-mole	Molar solution (M)	1
0·5 " "	Semi-molar solution $\left(\frac{M}{2}\right)$	$\frac{1}{2}=0{\cdot}5$
0·1 " "	Deci-molar solution $\left(\frac{M}{10}\right)$	$\frac{1}{10}=0{\cdot}1$
0·01 " "	Centi-molar solution $\left(\frac{M}{100}\right)$	$\frac{1}{100}=0{\cdot}01$

Molarity is the most common and universally accepted method of expressing concentration of a solution in analytical chemistry. Normality was previously used in analytical chemistry but of late it is superseded by molarity. This is because of the fact that equivalent weight is not constant but changes according to environment namely valency, oxidation number, acidity, basicity etc. But molecular weight of a substance is always constant. Thus the equivalent weight of $KMnO_4$ is 1/5th, 1/3rd or equal to molecular weight.

Hence how much quantity of solute is present in $\left(\frac{N}{10}\right)$ $KMnO_4$ is difficult to predict unless the reaction-condition is known. But the quantity of $KMnO_4$ in $\left(\frac{M}{10}\right)$ $KMnO_4$ solution is known with certainty. Therefore, a molar solution is clear and unambiguous but a normal solution is some what ambiguous.

(5) **Molality** *(m)* :

Molality denotes the number of moles of the solute dissolved in 1 kg (1000 g) of the solvent. Thus when 98 g of H_2SO_4 are dissolved in 1000 g of water, the molality of the solution is 1.

If 49 g of H_2SO_4 are dissolved in 1000 g of water, the molality of the solution = 0·5.

Let a g of solute of molecular weight M be dissolved in b g of solvent. Then number of moles of solute $= a/M$.

$\therefore$ b g of the solvent contain a/M moles of solute

or, 1000 g of the solvent contain $\frac{a\times 1000}{b\times M}$ moles of solute

$$\therefore \text{ Molality of the solution } = \frac{a\times 1000}{b\times M}$$

$$\text{i.e., Molality of the solution } = \frac{\text{Weight of the solute}\times 1000}{\text{Weight of the solvent}\times\text{molecular wt. of the solute}}$$

• **Molal solution :** *A molal solution is defined as a solution where 1 gram-mole of the solute is dissolved in 1 kg (1000 g) of the solvent.* It is denoted by the symbol "*m*".

Thus, *"0·1 (m) alcoholic solution of Urea"*—this statement means $\left(\frac{1}{10}\right)$th gram-mole of Urea is dissolved in 1000 g of alcohol.

• **Mole fraction :** *The mole fraction of a component in a solution is equal to the ratio of the number of moles of the component to the total number of moles of all the components in the solution.*

Let the number of moles of the solute in a solution = n and that of the solvent = N, then,

$$\text{Mole fraction of the solute} = \frac{n}{N+n}$$

$$\text{Mole fraction of the solvent} = \frac{N}{N+n}$$

- **Difference between Molar and Molal solution :**

Take two 1 litre volumeteric flasks. Add 1000 ml water upto the mark in the Ist flask. Then add 40 g or 1 gram-mole of NaOH and dissolve it by careful shaking of the flask. The resulting volume of the solution will be more than 1 litre. This is 1 (*m*) NaOH solution.

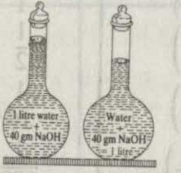


Fig 6.2 : Difference between molar & molal solution

In the second volumetric flask add first 40 g of NaOH and add water upto the mark. Dissolve the NaOH by careful shaking of the volumetric flask. Total volume of the solution is 1 litre. This is 1 (M) NaOH. Hence,

1 gram-mole of the solute + 1 litre (1000 g) water = 1 molal solution

1 gram-mole of the solute + water = 1 litre solution = 1 molar solution.

Since volume of water is more in molal solution, it can be reasonably concluded that 1 molar aqueous solution of a solute is stronger than its 1 molal aqueous solution. This is true whatever may be the solvent.

(6) **Formality :**

The formality of a solution is the number of gram-formula weight of the solute present in one litre of the solution. It is symbolised as "F"

The ionic solutes like NaCl, $MgCl_2$ etc., when dissolved in water are completely ionised. No descrete molecule of this type of solid is known in aqueous medium. These ionic compounds remain as ions even in the solid state. Again the aqueous solution of *barium hydroxide* does not contain any molecule which can be represented as $Ba(OH)_2.2H_2O$. Hence the term molecular weight is misnomer for such type of compounds as they do not exist as molecules. The term *formality* is, therefore, used to express their concentrations in aqueous medium instead of molarity.

- **Formal solution :**

A formal solution is a solution, 1 litre (1000 ml) of which contains 1 gram-formula weight of the solute.

The gram-formula weight of NaCl = 58·5 g and that of $Ba(OH)_2$ is 207 g. Hence 1(F) NaCl solution or 1(F) $Ba(OH)_2$ solution contains 58·5 g of NaCl and 207 g of $Ba(OH)_2$ respectively in 1 litre of solution.

Let m g of a solute of formula-weight F_w be dissolved in V litre of a solution.

Now V litre of the solution, contain m g of the solute.

∴ 1 litre of the solution, contain m/V g of the solute.

$$Formality = \frac{m/V}{F_w} = \frac{\text{Weight in gram of the substance per litre}}{\text{Gram-Formula weight}}$$

Weight of the substance in grams per litre of the solution

= Formula weight × Formality

Generally speaking, Formula weight and Molecular weight of a substance is the same. But if the molecular formula of the solute be the same as its formula representing the molecules present in its aqueous solution, then and only then formula wt. becomes equal to molecular wt. e.g., 0·1F soln. of ethyl alcohol of formula C_2H_5OH is equal to 0·1M soln. of ethyl alcohol. On the other hand 0·1F soln. of NaCl can not be regarded as its 0·1M soln. It should be expressed as 0·1M soln. in respect of Na^+ ions and 0·1M soln. in respect of Cl^- ions.

(7) **Percent strength :** *It is the number of gram of the solute present in 100 ml of the solution.* Thus 10% Na_2CO_3 solution means that 10 g of Na_2CO_3 are present in 100 ml of the solution. 15% HNO_3 soln. means that 15 g of HNO_3 are present in 100 ml of the solution.

[We know change in temperature causes change of volume of a liquid. Therefore, those concentration units which involve volume of solution must change with change in temperature. This explains why normality, molarity and formality vary with temperature. On the other hand, the terms molality, mole frection and PPM (Parts per million) are defined in term of weights of solute and solvents which are independent of temperature. Hence these concentration terms do not vary with temperature]

6.3. Conversion of strength of solution from one unit to other.

(1) From percent strength to normality and molarity.

- ***To express 5% NaOH solution in terms of normality and molarity :—***

5% NaOH means 100 ml of the solution contain 5 g of NaOH

or, 1000 ml of the solution contain 50 g of NaOH

Eq. wt. of NaOH = 40

Therefore, when 40 g of NaOH are present in 1000 ml of the soln. its strength is 1(N) when 50 g of NaOH are present in 1000 ml of the soln. its strength is $\frac{50}{40}$ (N)

Thus, when the strength of a solution is x% and the eq. wt. of the solute is E,

$$\textbf{Normality of the solution} = \frac{\textbf{Gram of the solute per litre}}{\textbf{Gram-eq. of the solute}}(N) = \frac{10x}{\textbf{Gram-eq. of the solute}}(N) = \frac{10x}{E}(N)$$

$$\text{Similarly, } \textbf{Molarity of the solution} = \frac{\textbf{Gram of the solute per litre}}{\textbf{Gram-molecular weight}}(M) = \frac{10x}{m}(M)$$

where m = **Gram-molecular weight of the solute.**

(2) (*a*) **From normality to percent strength :**

If the strength of a solution is x(N), then

$$\text{Per cent strength} = \frac{\text{Normality} \times \text{Gram-eq. of the solute}}{10}\ \%$$

$$\text{Thus per cent strength of } 0{\cdot}5\ (N)\ H_2SO_4 = \frac{0.5 \times 49}{10}\ \% = 2{\cdot}45\%$$

(*b*) **From molarity to percent strength :**

If the strength of a solution is x(M) then,

$$\text{Per cent strength} = \frac{\text{Molarity} \times \text{Gram-mole of the solute}}{10}\ \%$$

$$\text{Thus per cent strength of } 0{\cdot}5\ (M)\ H_2SO_4 = \frac{0.5 \times 98}{10}\ \% = 4{\cdot}9\%$$

(3) (*a*) **From normality to gram per litre :**

As already mentioned *Gram per litre = Normality × Eq.wt. of the solute*

$$\text{The normality of } \left(\frac{N}{5}\right) H_2SO_4 = \frac{1}{5}$$

$$\therefore \text{Gram of } H_2SO_4 \text{ per litre of the solution} = \frac{1}{5} \times 49 = 9{\cdot}8 \text{ gram/litre}$$

Similarly 0·5(N) Na_2CO_3 when expressed in gram per litre becomes $0{\cdot}5 \times 53 = 2{\cdot}65$ gram/litre.

(b) **From molarity to gram per litre :**
We know,
Gram of solute per litre of the solution = Molarity × Mol. wt.

Thus $\left(\frac{M}{5}\right)$ H_2SO_4 has molarity $= \frac{1}{5}$

Hence, gram of H_2SO_4 per litre $= \frac{1}{5} \times 98 = 19{\cdot}6$ gram/litre

(4) (a) **From gram per litre to normality :**

$$\text{Normality of the solution} = \frac{\text{Gram of the solute per litre}}{\text{Gram-eq. of the solute}}$$

(b) **From gram per litre to molarity :**

$$\text{Molarity of the solution} = \frac{\text{Gram of the solute per litre}}{\text{Gram-mole of the solute}}$$

(5) **From molarity to normality :**

We know 2(M) H_2SO_4 means $2 \times 98 = 196$ g of H_2SO_4 are present in 1 litre of the solution.

Again 4(N) H_2SO_4 means $4 \times 49 = 196$ g of H_2SO_4 are present per litre of the solution.

Therefore, 2(M) $H_2SO_4 \equiv$ 4(N)H_2SO_4

Thus when the molarity of an acid solution is multiplied by the basicity of the acid or by the number of replaceable H^+ ions of the acid, the strength of the acid solution will be expressed in normality. Thus 3(M) $H_2SO_4 = 3 \times 2 =$ 6(N) H_2SO_4

When the molarity of an alkali solution is multiplied by the acidity of the alkali, the strength of the alkali solution is obtained in terms of normality.

Thus 3 (M) $Ca(OH)_2$ = 3×2 = 6(N) $Ca(OH)_2$ solution.
0·1 (M) NaOH = $0{\cdot}1 \times 1$ = 0·1 (N) NaOH solution.

(6) **From normality to molarity :**

Molarity of a solution results when the normality of an acid or base is divided by basicity of the acid or acidity of the base respectively.

Thus 0·2 (N) $Na_2CO_3 = \frac{0{\cdot}2}{2}$ (M) = 0·1 (M) Na_2CO_3 solution

0·5 (N) $H_2SO_4 = \frac{0{\cdot}5}{2}$ (M) = 0·25 (M) H_2SO_4 "

In General :

$$\textit{Molarity of a solution} = \textit{Normality of the solution} \times \frac{\textit{Eq. wt. of the solute}}{\textit{Mol. wt. of the solute}}$$

$$\textit{Normality of a solution} = \textit{Molarity of the solution} \times \frac{\textit{Mol. wt. of the solute}}{\textit{Eq. wt. of the solute}}$$

e.g., If the molarity of H_2SO_4 solution is 2(M) then its normality $= 2 \times \frac{98}{49} = 2 \times 2$ 4(N).

(7) **To express strength in normality or molarity from density or specific gravity of the soultion and percent by weight of the solute in solution :**

Sometimes the strength of an acid or base is expressed in percent strength. Percent strength indicates the weight in gram of the solute per 100 g of the solution. Thus 98% H_2SO_4 denotes that 98 g of H_2SO_4 is present in 100 g of the solution. If the specific gravity of the solution is given then the strength of the resulting solution in gram per litre or normality or molarity can be evaluated in accordance with the following procedure.

Thus *if a bottle is marked 98% H_2SO_4 and specific gravity = 1·14, its strength in the above 3 units can be expressed as follows :—*

(i) Since the specific gravity = 1·14
The weight of 1 ml solution is 1·14 g
or, „ „ 1000 „ „ 1·14 × 1000 = 1140 g
The solution is 98%.
Hence 100 g of the solution contain 98 g of H_2SO_4

$$\therefore \quad 1140 \text{ " " " "} \quad \frac{98 \times 1140}{100} = 1117{\cdot}2\,\text{g}$$

or, 1000 ml of H_2SO_4 contains 1117·2 g of H_2SO_4

$$\text{Hence, normality of the solution} = \frac{\text{Weight of solute per litre of solution}}{\text{Eq. wt. of solute}}$$

$$= \frac{1117{\cdot}2}{49} = 22{\cdot}8$$

Hence the strength of H_2SO_4 = 22·8 (N)

(ii) The gram molecular weight of H_2SO_4 = 98 g

$$\text{The Molarity of the solution} = \frac{\text{Weight of } H_2SO_4 \text{ per litre of solution}}{\text{Mol. weight of } H_2SO_4}$$

$$= \frac{1117{\cdot}2}{98} = 11{\cdot}4$$

or, the strength of the H_2SO_4 solution = 11·4 (M)

While working problems on volumetric analysis remember the following formulae :

(i) Gram/litre = Normality × Gram Eq. wt. of the solute
(ii) Gram/litre = Molarity × Gram moles of the solute
(iii) Molarity = Its Normality × $\dfrac{\text{Eq. wt. of the solute}}{\text{Gram-mol. wt. of the solute}}$
(iv) Normality = Its Molarity × $\dfrac{\text{Molecular weight of the solute}}{\text{Eq. wt. of the solute}}$
(v) % of the solute in the solution = $\dfrac{\text{Normality} \times \text{Gram Eq. wt}}{10}$
(vi) % of the solute in the solution = $\dfrac{\text{Molarity} \times \text{Gram-Molecular weight}}{10}$
(vii) Normality = $\dfrac{\text{\% of the solute} \times 10}{\text{Eq. wt. of the solute}}$
(viii) Molarity = $\dfrac{\text{\% of the solute} \times 10}{\text{Gram Molecular weight}}$
(ix) Number of moles = Number of litres × Molarity
(x) Number of Millimoles = Number of millilitres × Molarity.

6.4. Neutralisation.

Whenever acids and bases combine together in the ratio of their equivalent weights, salts and water are formed quantitatively. The resulting solution is neutral and this type of reaction is called *neutralisation*. Both acids and bases lose their identities completely.

According to Ionic theory, neutralisation amounts to the formation of undissociated weak electrolyte H_2O by the interaction of H^+ ions [or $(H_3O)^+$ ions] of the acid and OH^- ions of the alkalis.

$$H^+ + OH^- \rightleftharpoons H_2O$$
$$H_2O + H^+ = [H_3O^-]$$

The reactant-ratio being gram eq. of H^+ ions and gram eq. of OH^- ions in aqueous medium, the pH of the medium is 7.

Thus gram equivalents ratio of HCl and NaOH react to form NaCl and H_2O

$$NaOH + HCl = NaCl + H_2O$$

Both NaOH and HCl being strong electrolyte dissociate completely in aqueous medium. Since the reactants are in the ratio of their equivalent weights, H^+ ions of acid and OH^- ions of the base combine to form undissociated H_2O molecules $H^+ + OH^- \rightleftharpoons H_2O$. The solution contains neither excess H^+ ions nor excess OH^- ions. The solution is neutral at this point which is referred to as neutralisation point where acid and base neutralise each other. The cations of the base and anions of the acid remain unchanged in solution.

$$\begin{array}{rcl} HCl & \rightleftharpoons & H^+ + Cl^- \\ NaOH & \rightleftharpoons & Na^+ + OH^- \\ \hline NaOH + HCl & \rightleftharpoons & H_2O + (Na^+ + Cl^-) \end{array}$$

Acidimetry : *Acidimetry is a process of determining the unknown strength of an alkali with a known strength of an acid by titrating with a suitable indicator.*

Alkalimetry : *Alkalimetry is just the opposite to Acidimetry. It is a process of determining the unknown strength of an acid with a known strength of an alkali by titrating with a suitable indicator.*

(Some Analytical chemists, however, support the opposite view of the definition expressed here.)

- **Titration :**

Titration is an operation of determining the volume of a solution of a unknown strength which is required to react completely with a definite volume of a standard solution in presence of a suitable indicator.

In carrying out any titration, a known volume (generally 25 ml) of one of the solutions is taken in a conical flask and the other solution is taken in a burette. The solution in the burette is slowly and carefully added to the solution in the conical flask till the end-point is reached i.e., the reaction is just complete. To find out this end-point a suitable indicator is used. The volume of the solution added from the burette is noted. Now if the strength of one of the solutions is known, the strength of the other can be calculated as follows.

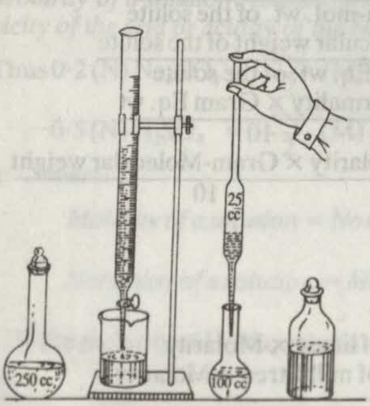


Fig 6.3 :

Let the strength of an acid be S_1 (N). Let V_1 ml of this acid be required for the titration of V_2 ml of an alkali whose strength is S_2 (N) is unknown.

Therefore V_2 ml of S_2 (N) alkali $\equiv V_2S_2$ ml of (N) alkali

Again V_1 ml of S_1 (N) acid $\equiv V_1S_1$ ml of (N) acid.

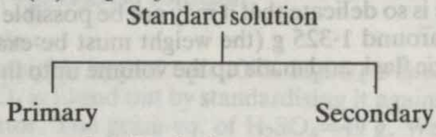
Since the solution of an acid and an alkali of the same strength neutralise each other in equal volumes.

$$\therefore\ V_1S_1 = V_2S_2 \qquad \text{or,} \quad S_2 = \frac{V_1S_1}{V_2}$$

If the strength of the acid solution S_1 and the volume of acid and alkali being known, the strength of alkali S_2 can be easily found out.

6.5. Standard solution.

A solution of known strength used in volumetric analysis is called a standard solution. Thus 0·1 (N) Na_2CO_3 is a standard solution as strength is known.



[A] Primary standard solution :

There are some substances which can be obtained in the pure and dry state. The accurate weight of these substances can be found out by weighing them in a chemical balance. Furthermore, these substances do not suffer any chemical change even if they are exposed to the atmosphere for a prolonged period of time. Such substances are known as primary standard substances e.g., anhydrous Na_2CO_3, oxalic acid, $K_2Cr_2O_7$, Borax etc. *A standard solution of such substance can be prepared by dissolving a known weight of it in a known volume of water. The standard solution thus prepared is called a primary standard solution.*

Characteristics of a Primary standard substance.

A primary standard substance (i) must be available in pure and dry condition. (ii) During weighing in a chemical balance it should not undergo any change in contact with air. (iii) Its equivalent weight should be high, to reduce weighing error. (iv) It should not be hygroscopic. (v) It should be highly soluble in water. (vi) Its reactions in aqueous medium should be instantaneous. (vii) The impurities present in it, should not exceed 0·01 percent. (viii) It should not react with water or CO_2 or air. It should not change its weight on exposure to air, by volatilisation, deliquescence, loss of water of crystalisation. (ix) The strength of its solution should not change at all even if it is kept for long time. (x) It must react in one way only under the conditions of titration ; there must be no side reaction.

[B] Secondary standard solution :

There are some substances which are not readily available in pure and dry condition. Some of them are hygroscopic. Some react with air or slowly decompose by light. Hence their accurate weight can not be found out by weighing them in a chemical balance. So the exact weight of the solute present in a definite volume of water is not known precisely. Moreover, their concentrations slowly change when kept even in air tight volumetric flasks. These substances are referred to secondary standard substances" e.g., H_2SO_4, CH_3COOH, NaOH, HCl, KOH, $KMnO_4$, $Na_2S_2O_3$ etc. In such case a solution of approximate strength is first prepared by dissolving an approximate weight of such substance in a definite volume of water. The solution thus prepared is then titrated with a primary standard solution using a suitable indicator to know its exact strength.

Hence *a secondary standard solution is a solution whose accurate strength is determined indirectly by titrating against a primary standard solution.*

6.6. Preparation of Primary standard solution of $\left(\frac{N}{10}\right)$ Na_2CO_3.

To prepare 250 ml of $\left(\frac{N}{10}\right)$ Na_2CO_3 solution.

[A] Principle :

The gram-eq. of $Na_2CO_3 = 53$ g

Consequently 1 litre of $\left(\frac{N}{10}\right)$ Na_2CO_3 solution requires exactly 5·3 g of Na_2CO_3

$\therefore$ 250 ml of $\left(\frac{N}{10}\right)$ Na_2CO_3 require $\frac{5 \cdot 3}{4} = 1 \cdot 325$ g of Na_2CO_3.

Now a chemical balance is so delicate that it may not be possible to weigh exactly. 1·325 g. Hence a weight around 1·325 g (the weight must be exact) of Na_2CO_3 is taken in a 250 ml volumetric flask and made up the volume upto the mark by adding water.

[B] Procedure :

A clean 250 ml standard volumetric flask is taken and a funnel is placed in its mouth. Pure anhydrous Na_2CO_3 is taken in a weighing bottle and the bottle together with Na_2CO_3 is accurately weighed in a chemical balance. The weight is noted. Let it be W_1 g. Now some Na_2CO_3 is split into the funnel from the bottle carefully, making a guess that the split amount is around 1·325 g. The bottle is transferred to the left pan of the balance and weight of it is taken. If the split amount is too low, the process is repeated till the weight comes around 1·325 g. Now the bottle is carefully weighed again. Let this weight be W_2 g. The difference $(W_1 - W_2)$ g is the amount of Na_2CO_3 transferred in the volumetric flask. The Na_2CO_3 adhered on the funnel is washed down with distilled water into the flask. The funnel is then removed. Adding a little more distilled water, the flask is shaken to make the solution homogeneous and finally the volume is made upto the mark.

[C] Calculation :

When 250 ml of the solution contain 1·325 g, the strength is $\left(\frac{N}{10}\right)$

When 250 ml solution contains $(W_1 - W_2)$ g the strength is $\frac{W_1 - W_2}{1 \cdot 325}$ (N/10)

$\left(\frac{W_1 - W_2}{1 \cdot 325}\right)$ is called the factor.

The strength of the solution can also be expressed in normality as follows :—

$$\frac{(W_1 - W_2) \times 4}{53} \text{ (N)}$$

- **Preparation of exact decinormal solution of Na_2CO_3 :**

To prepare exact decinormal solution of Na_2CO_3, the best method is to weigh exactly 1·325 g of Na_2CO_3 and prepare the solution as given above [$(W_1 - W_2) =$ 1·325 g]. Another process may be recommended though not normally followed in the laboratory. In this case the weight of Na_2CO_3 taken must be slightly higher than 1·325 g i.e., $(W_1 - W_2) > 1 \cdot 325$ g. It is dissolved in water as described above. The water level is just at 250 ml mark. The strength of such solution is $\frac{(W_1 - W_2)}{1 \cdot 325}\left(\frac{N}{10}\right)$ and its volume = 250 ml.

To convert 250 ml of this strength to exact N/10 solution let the volume is to be increased to V ml.

$$\therefore\ V \times \frac{N}{10} = 250 \times \frac{(W_1 - W_2)}{1{\cdot}325}\left(\frac{N}{10}\right)$$

$$\text{or,}\quad V = \frac{250 \times (W_1 - W_2)}{1{\cdot}325}\ \text{ml.}$$

Hence by adding $(V - 250)$ ml of distilled water to the 250 ml solution in the volumetric flask, the solution is made exactly $\left(\frac{N}{10}\right)$.

6.7. Preparation of Secondary standard solution.

To prepare $\left(\frac{N}{10}\right)$ H_2SO_4 solution.

[A] Principle :

Since H_2SO_4 is highly hygroscopic 100% H_2SO_4 is never found. Therefore correct strength of H_2SO_4 is found out by standardising it against a primary standard using a suitable indicator. The gram-eq. of H_2SO_4=49 g. We know if 4·9 g of H_2SO_4 is present in 1000 ml solution its strength will be $\left(\frac{N}{10}\right)$. Since H_2SO_4 is hygroscopic its weight can not be found out by direct weighing in a chemical balance. The weight is calculated by indirect means.

From the density of H_2SO_4 and by using *Lunge's table* the percentage of H_2SO_4 in the solution of that density can be found out.

[B] Calculation :

Let the density of the $H_2SO_4 = d$ g/ml and its percentage strength$=x$%

$\therefore$ Weight of 1000 ml of H_2SO_4 solution$=1000d$ g.

Again 100 g H_2SO_4 solution contain x g of H_2SO_4

$$\therefore\ 1000\,d\text{ g } H_2SO_4 \text{ solution contain } \frac{x \times 1000d}{100}$$

$$= 10d \times x \text{ g of } H_2SO_4$$

This weight of H_2SO_4 is present in 1000 ml solution.

$$\therefore\ \text{the strength of } H_2SO_4 = \frac{10d \times x}{49}\ (N)$$

Let V ml of H_2SO_4 of this strength is required to prepare 1000 ml of $\left(\frac{N}{10}\right)$ solution.

$$\therefore\ V \times \frac{10d \times x}{49}(N) = 1000 \times \frac{N}{10}$$

$$V = \frac{100 \times 49}{10d \times x} = \frac{490}{d \times x}\ \text{ml.}$$

[C] Procedure :

The given acid is taken in a burette. The acid level is noted. Now $\frac{490}{dx}$ ml of the acid is added into a standard 1 litre flask, half filled with distilled water and the flask is shaken. Water is added slowly in the flask upto the mark and the solution in the stoppered 1 litre flask is tilted upside down 3-4 times to make uniform. The strength of the solution is around $\left(\frac{N}{10}\right)$. Now titrate an aliquot of it against standard $\left(\frac{N}{10}\right)$ Na_2CO_3 solution using Methyl orange indicator. The exact strength of H_2SO_4 is found out.

Example : Let the density of the given H_2SO_4=1·84 g/ml and it is 97% pure.

$\therefore$ Wt. of 1000 ml of H_2SO_4 solution=1840 g.

Again 100 g of H_2SO_4 solution contain 97 g of pure H_2SO_4

$$1840 \text{ g of } H_2SO_4 \text{ solution contain } \frac{97\times1840}{100} = 1784{\cdot}8 \text{ g of pure } H_2SO_4$$

$$\therefore \text{ Strength of } H_2SO_4 = \frac{1784{\cdot}8}{49}\,(N) = 36{\cdot}4245\,(N)$$

Let V ml of this acid is required to prepare 1000 ml of $\left(\frac{N}{10}\right) H_2SO_4$

$$\text{or, } \quad V\times36{\cdot}4245\,(N) = 1000\times\frac{N}{10} \qquad V = \frac{1000}{36{\cdot}4245\times10} = 2{\cdot}745 \text{ ml.}$$

Now add 2·8 ml of this H_2SO_4 by a measuring cylinder into 1 litre volumetric flask which is already half filled with water. Make up the volume upto the mark. Shake well. The resulting solution is around $\left(\frac{N}{10}\right) H_2SO_4$.

N/10 solutions of HCl, HNO_3 are prepared by the same method.

6.8. Titration Process.

Standardisation of $\left(\frac{N}{10}\right)$ H_2SO_4 against standard Na_2CO_3 solution.

1. Apparatus : 50 ml burette, 25 ml pipette, a conical flask, burette stand and a wash bottle.

2. Chemicals : A standard solution of $\left(\frac{N}{10}\right) Na_2CO_3$ of known strength and a secondary standard solution of H_2SO_4 whose strength is to be found out.

3. Indicator : *Methyl orange.*

4. Procedure : (i) A 50 ml burette is first washed with chromic acid and then washed several times with distilled water. It is then rinsed twice with the acid solution. The burette is filled up with the acid solution upto the zero mark. Care must be taken so that no air bubble is left inside the burette and lower portion of the burette should not be empty (Fig 6·4) It is then clamped to a stand vertically. (ii) The 25 ml pipette is washed twice with distilled water and then rinsed with the standard $\left(\frac{N}{10}\right) Na_2CO_3$ solution.

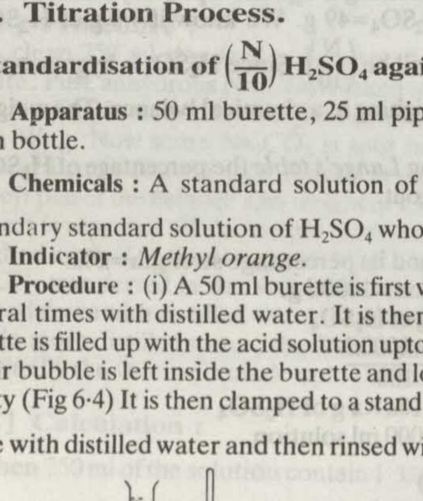


Fig 6.4 : Titration process

Now 25 ml of the (N/10) Na_2CO_3 solution is taken out by means of the pipette and transferred it into the conical flask, which is already well washed by distilled water. The last drop of Na_2CO_3 solution adhered to the pipette is not transferred by blowing. The end of the pipette is touched to the inner wall of the conical flask. (iii) One or two drops of methyl orange are added to this solution when it turns *yellow.* (iv) Now the acid solution from the burette is slowly added to the alkali solution and the flask is continuously shaken during the addition of H_2SO_4. Since the acid is also of (N/10) order, nearly 25 ml of the acid will be required for complete neutralisation. Hence about 20 or 21 ml of the acid are added at a time into the conical flask and then added drop by drop until the colour of the alkali solution just changes from yellow to orange. This is the end-point. The addition of acid is stopped and the burette reading is noted. This process is repeated thrice and the mean volume of the acid is found out.

5. Calculation :

Let the strength of the acid is S_1 and the volume of the acid required V_1 ml

$$V_1 \times S_1 = 25 \times \frac{\mathrm{N}}{10}$$

$$S_1 = \frac{25}{V_1 \times 10} \text{ (N)}$$

6.9. Indicators.

Generally, an indicator is a chemical which is used to indicate the presence of a chemical substance or ion either by the change of its colour or by producing turbidity or Fluorescence. In volumetric analysis such substances indicate the end point of titration.

Indicators are of 3 types (a) *Acid base or Neutralisation indicator,* (b) *Redox indicator,* (c) *Adsorption indicator.* Neutralisation or Acid-base indicators are used in acidimetry and alkalimetry and indicate by change of its colour whether a solution is acidic, alkaline or neutral. Indicators are either weak organic acids or bases. Thus *phenolphthalein is a weak organic acid* while *methyl orange is a weak organic base.* The former can detect the end point of titration between a *weak acid* and *strong base* while the latter can indicates the end print of titration between a weak base and strong acid. Some of them can be prepared synthetically and the others can be obtained from natural source. An indicator should not interfere with the reaction. The colour of some indicators are shown in the following table.

Indicator	Colour in Acids	Colour in neutral solution	Colour in alkalis
Methyl orange	Red	Orange	Yellow
Litmus	Red	Violet	Blue
Phenolphthalein	Colourless	Colourless	Pink
Methyl red	Red	Orange	Yellow

It is to be remembered that all indicators cannot be used for all types of acid-base titration. The choice of an indicator depends on the nature of acid and base as also the H^+ ion of the solution near the end-point (For theories and choice of acid base indicator see chapter on Ionic equilibrium.

Selection of indicators :

The selection of a suitable indicator to get the correct end-point in a neutralisation reaction is very essential. It is known that in a neutralisation reactions equivalent amounts of an acid and an alkali react completely to produce salt and water. The salt thus produced may or may not be exactly neutral. Due to the hydrolysis of the salt, the solution of the salt may either be slightly acidic or alkaline. The neutralisation reaction between a strong base and a weak acid e.g., (NaOH and CH_3COOH) forms a salt which undergoes hydrolysis producing a slightly alkaline solution at the end-point. Consequently in this case phenolphthalein is suitable as it changes its colour in alkaline solution. For the same reason neutralisation between a strong acid and weak base (e.g., H_2SO_4 and Na_2CO_3) gives a slightly acidic solution at the end-point. In this case methyl orange is suitable as it changes its colour in acidic solution. The neutralisation between a strong acid and a strong base forms a salt which does not suffer hydrolysis. Consequently at the end-point the resulting solution is exactly neutral and so any indicators can be used for such case.

Suitability of indicators :

Titration of		Examples of Neutralisation	Indicator to be used
Acid	Base		
1. Strong	Strong	$HCl + NaOH$	Any Indicator
2. Strong	Weak	$HCl + NH_4OH$ $HCl + Na_2CO_3$	Methyl orange, Methyl red
3. Weak	Strong	$CH_3COOH + NaOH$	Phenolphthalein
4. Weak	Weak	$CH_3COOH + NH_4OH$	No suitable indicator

• While selecting an indicator for an acid base titration the following point are to be noted :

(i) If in any reactions CO_2 is evolved methyl orange indicator should be used. (ii) Phenolpthalein indicator should not be used if ammonia is evolved in any reaction. (iii) When phenolpthalein is used in the neutralisation of Na_2CO_3 and a strong acid e.g., HCl, H_2SO_4, the pink colour of the Na_2CO_3 solution becomes colourless when only half of the Na_2CO_3 is neutralised. This is because of the fact that the reaction of Na_2CO_3 with strong acid takes place two stages. In the first stage the whole of Na_2CO_3 is converted to $NaHCO_3$. In the second stage the $NaHCO_3$ thus produced reacts with the acid and is completely neutralised to form normal salt. As $NaHCO_3$ is an acid salt, its alkalinity is not exhibited by phenolpthalein indicator and as result the pink colour of the solution disappears at this stage.

$$\begin{aligned} Na_2CO_3 + HCl &= NaHCO_3 + NaCl \\ NaHCO_3 + HCl &= NaCl + CO_2 + H_2O \end{aligned}$$

The end-point of the neutralisation of bicarbonate can be found out by using methyl orange indicator. It has been found that by using phenolphthalein indicator the volume of acid required to reach the end-point of the first stage of reaction i.e., $Na_2CO_3 \rightarrow NaHCO_3$ is equal to the volume of acid required to neutralise completely the produced $NaHCO_3$ using methyl orange indicator.

How to distinguish between Na_2CO_3 and $NaHCO_3$?

To an aqueous soln. of $NaHCO_3$ when two drops of phenolpthalein are added, no change of colour of the solution is observed. On the other hand when two drops of phenolpthalein are added to an aqueous solution of Na_2CO_3 the colourless soln. turns violet red.

3. Litmus can not be used when a carbonate or bicarbonate is titrated with an acid because the liberated CO_2 imparts a red tint to litmus solution before the end-point is reached.

[Other types of Indicator can be used for other reaction e.g., in Iodimetry or Iodometry, starch is a suitable indicator because of the deep blue complex it forms with iodine. Diphenyl amine is a redox indicator used in the estimation of Fe^{++} by $K_2Cr_2O_7$ solution. Redox indicators are chemicals that show a reversible colour change between oxidised and reduced forms. Adsorption indicators, on the other hand show colour change on the surface of the precipitate but not in the solution. Some of the example of adsorption indicators are Fluorescein, Alizarin Red etc.]

Criteria of a good indicator : A good indicator must have the following properties—

(i) The indicator must indicate a sharp change in colour at the point of neutralisation.

(ii) The colours of the indicator in acid and alkaline solutions must be permanent and contrasting to each other.

(iii) The change of colour should occur at a very small difference of H^+ ion concentration of the solution.

6.10. A Few Principles of Acidimetry and Alkalimetry.

1. **The volume of a solution can be altered by keeping the products of the volume and Normality constant.**

$$1 \text{ ml (N) solution} \equiv x \text{ ml of} \left(\frac{N}{x}\right) \text{solution} \equiv y \text{ ml of} \left(\frac{N}{y}\right) \text{solution}$$

(where x and y are any number)

$$\text{Thus } 5 \text{ ml of} \left(\frac{N}{5}\right) H_2SO_4 \equiv 10 \text{ ml of} \left(\frac{N}{10}\right) H_2SO_4 \equiv 50 \text{ ml of} \left(\frac{N}{50}\right) H_2SO_4$$

Thus, y ml of x (N) soln. $\equiv$ ($y \times x$) ml of (N) soln. $\equiv$ x ml of y (N) soln.

Thus as the normality of the solution decreases the volume containing 1 gram equ. increases. i.e., volume of a solution is inversely proportional to its strength in terms of normality.

2. *Equal volumes of solutions of acids and alkalies of same normality exactly neutralise each other.*

From the Law of equivalent proportion it is evident that *1 gram eq. of an acid neutralise 1 gram eq. of any alkali.*

or, x ml of 1 (N) acid will neutralise x ml of 1 (N) alkali

or, 5 ml of $\left(\frac{N}{10}\right)$ NaOH will neutralise 5 ml of $\left(\frac{N}{10}\right)$ HCl solution

or, *Equal volumes of x (N) acid and x (N) alkali will neutralise each other.*

3. *During neutralisation equal volumes of acid and alkali of same strength must neutralise each other, consequently,*

$$\frac{\text{Volume of acid}}{\text{Volume of alkali}} = \frac{\text{Strength of alkali in normality}}{\text{Strength of acid in normality}}$$

or, $V_1 \times S_1 = V_2 \times S_2$

V_1 = Volume of acid, V_2 = Volume of alkali

S_1 = Strength of acid in normality, S_2 = Strength of alkali in normality.

(This equation is applicable when the strength of the solution are expressed in terms of normality).

4. *1 Equivalent ≡ Equivalent weight expressed in gram*

or, **1000 milli equivalent (m eq.) ≡ 1 equivalent ≡ Eq. wt. expressed in gram.**

Thus, 1000 milli eq. of NaOH = 40 g of NaOH

or, 1 milli eq. of NaOH = 0·04 g of NaOH

Similarly 1 milli eq. of Na_2CO_3 = 0·053 g of Na_2CO_3

1 milli eq. of HCl = 0·0365 g of HCl.

6.11. Numercial examples.

[A] Calculation of weight of solute from the volume and strength of solution :

1. *Determine the weight of solute in the following solutions :*

(*a*) *400 ml of 1·25* $\left(\frac{N}{10}\right)$ *Na_2CO_3 solution.*

(b) 400 ml of 0·25 (M) Na_2SO_4 solution.
(c) 600 ml of 10% $Ca(OH)_2$ solution.
(d) 2·3 litre of 0·9 (N) NH_4Cl solution.
(e) 200 ml of (M/2) H_2SO_4 solution.

Ans : (a) Gram eq. wt. of $Na_2CO_3 = \dfrac{106}{2} = 53$ g

Weight of Na_2CO_3 present per litre of the solution $= 1{\cdot}25 \times \dfrac{53}{10} = 6{\cdot}625$ g

$\therefore$ 1000 ml solution contain 6·625 g of Na_2CO_3

400 ml solution contain $\dfrac{6{\cdot}625 \times 400}{1000} = 2{\cdot}65$ g of Na_2CO_3

(b) Gram mol. wt. of $Na_2SO_4 = 142$ g
1 litre of 0·25 (M) Na_2SO_4 contain $= 0{\cdot}25 \times 142 = 35{\cdot}5$ g
1000 ml of the solution contain 35·5 g Na_2SO_4
400 ml of the solution contain $\dfrac{35{\cdot}5 \times 400}{1000} = 14{\cdot}2$ g

(c) 100 ml of 10% $Ca(OH)_2$ solution contain 10 g $CaOH)_2$
600 ml of 10% $Ca(OH)_2$ solution contain $\dfrac{10 \times 600}{100} = 60$ g

(d) Gram-equivalent weight of $NH_4Cl = \dfrac{53{\cdot}5}{1} = 53{\cdot}5$ g
1 litre of 0·9 (N) NH_4Cl contain $0{\cdot}9 \times 53{\cdot}5 = 48{\cdot}15$ g
1 litre of solution contains 48·15 g NH_4Cl
2.3 litre of solution contains $48{\cdot}15 \times 2{\cdot}3 = 110{\cdot}745$ g NH_4Cl

(e) Gram Mol weight of $H_2SO_4 = 98$ g
1 Litre $\left(\dfrac{M}{2}\right)$ H_2SO_4 contains $98 \times \frac{1}{2} = 49$ g
1000 ml solution of H_2SO_4 contain 49 g of H_2SO_4
200 ml solution of H_2SO_4 contain $\dfrac{49 \times 200}{1000} = 9{\cdot}8$ g of H_2SO_4

[B] To express concentration in different units from the volume of the solution and weight of the solute.

2. *Determine the concentration of the following solutions in terms of Normality and Molarity.*
(a) 1·358 g of H_2SO_4 in 250 ml solution.
(b) 10 g of NaOH (95% pure) in 200 ml solution.
(c) 5% NaOH solution.

Ans : (a) (i) Gram eq. of $H_2SO_4 = 49$ g
250 ml of H_2SO_4 contains 1·358 g
1000 ml of H_2SO_4 contains $\dfrac{1{\cdot}358 \times 1000}{250} = 5{\cdot}432$ g
49 g of H_2SO_4 in 1000 ml solution = 1(N) H_2SO_4
5·432 g of H_2SO_4 in 1000 ml solution $= \dfrac{5{\cdot}432}{49}(N) = 0{\cdot}1108(N)$ H_2SO_4

(ii) Again
98 g of H_2SO_4 in 1000 ml solution = 1(M) H_2SO_4
5·432 g of H_2SO_4 in 1000 ml solution $= \dfrac{5{\cdot}432}{98} = 0{\cdot}0554(M)$ H_2SO_4

(b) (i) 100 g of NaOH contain 95 g pure NaOH
10 g of NaOH contain 9·5 g pure NaOH
∴ 200 ml of the solution contains 9·5 g pure NaOH

∴ 1000 ml of the solution contains $\frac{9.5 \times 1000}{200} = 47{\cdot}5$ g NaOH

∴ Strength = $\frac{47{\cdot}5}{40}$ (N) = 1·1875 (N)

(ii) The acidity of NaOH = 1, hence gram-eq. of NaOH = gram-mole of NaOH.
Or, Normality = Molarity.
Hence the strength of NaOH = 1·1875 (M)

(c) 5% NaOH means— 100 ml solution contain 5 g of NaOH
∴ 1000 ml solution contains 50 g of NaOH

∴ Strength of NaOH = $\frac{50}{40}$ (N) = 1·25 (N)

Molarity is also 1·25 (M) as NaOH is mono acidic.

[C] Change of concentration of the solution by the addition of known volume of water i.e., reduction of strength.

3. *(a) 200 ml of 5 (N) H_2SO_4 is mixed with 800 ml of distilled water. Express the strength of the resulting solution.*

(b) To 100 ml of 2 (M) Na_2CO_3 water is added. The total volume of the solution becomes 500 ml. Calculate the normality and molarity of the resulting solution.

(c) 500 ml of 10% NaOH is added to water to make the volume 1 litre. Calculate the strength of the resulting solution in normality and molarity.

Ans. : (a) The total volume of the diluted solution = (200 + 800) = 1000 ml.
Let the concentration of the diluted solution be x (N).
Hence $1000 \times x$ (N) = 200×5 (N)
or, $x = 1$ (N)
The strength the resulting solution = 1 (N)
Since the basicity of H_2SO_4 =2, the molarity = 1/2 = 0·5 (M)

(b) The volume of the diluted solution is 500 ml. Let its strength be x.
∴ $500 \times x = 100 \times 2$ (M)

$x = \frac{100 \times 2}{500}$ (M) = 0·4 (M)

∴ Strength of the diluted Na_2CO_3 solution is 0·4 (M) = 0·8 (N)
Since the gram-eq. weight of Na_2CO_3 = 1/2 × Gram molecular weight of Na_2CO_3.

(c) 100 ml of NaOH contain 10 g of NaOH
1000 ml of NaOH contain 100 g of NaOH

∴ Strength of NaOH solution = $\frac{100}{40}$ (N) = 2·5 (N)

The volume of the diluted solution = 1000 ml.
Let the strength of the diluted solution be x(N)
∴ $1000 \times x$(N) = 2·5(N) × 500

$x = \frac{2.5 \times 500}{1000}$ (N) = 1·25 (N)

Normality of the solution = 1·25 (N)
∴ Molarity of the solution = 1·25 (M)
Since the gram-eq. of NaOH = gram mole of NaOH

[D] To calculate the volume of a solution of known strength which contains a known weight of solute :

4. *(i) Calculate the volume of $\left(\frac{N}{10}\right)$ H_2SO_4 that contains 3.92 g of H_2SO_4*

(ii) What is the volume of solution of 0·65 (N) containing 6 g of NH_4Cl ?
(iii) Calculate the volume of 0·5 (M) Na_2CO_3 which contains 0·53 g of Na_2CO_3.

Ans : (i) 1000 ml of $\left(\frac{N}{10}\right)$ H_2SO_4 contains 4·9 g of H_2SO_4
or, 4·9 g of H_2SO_4 is present in 1000 ml solution.
∴ 3·92 g of H_2SO_4 is present in $\frac{1000\times3\cdot92}{4\cdot9} = 800$ ml.

(ii) The gram eq. of $NH_4Cl = 53\cdot5$ g
1000 ml of 0·65(N) solution of NH_4Cl contain $0\cdot65\times53\cdot5 = 34\cdot77$ g
or, 34·77 g of NH_4Cl are present in 1000 ml
6 g of NH_4Cl are present in $\frac{1000\times6}{34\cdot77} = 172\cdot56$ ml

(iii) Gram-molecular weight of $Na_2CO_3 = 106$ g
1000 ml of 0·5(M) Na_2CO_3 solution contain $0\cdot5\times106 = 53$ g
∴ Required volume of the solution $= \frac{1000\times0\cdot53}{53} = 10$ ml

[E] To express the strength of a solution in (i) Normality, (ii) Molarity from density or specific gravity of the solution and percentage of solute in the solution.

5. *The density of a concentrated solution of H_2SO_4 is 1·84 g/ml and it contains 98% by weight of the acid. Find the normality and molarity of the acid.*

Ans : Given density of the acid = 1·84 g/ml
∴ Weight of 1 ml acid = 1·84 g
or, Weight of 1000 ml acid = 1840 g
The acid contains 98% of pure H_2SO_4
100 g of the acid contain 98 g of pure H_2SO_4
1840 g of the acid contain $\frac{98\times1840}{100} = 1803\cdot2$ g
∴ 1000 ml of the H_2SO_4 solution contain 1803·2 g of H_2SO_4.
Hence the strength of H_2SO_4 in normality $= \frac{1803\cdot2}{49} = 36\cdot8$ (N)
Strength of H_2SO_4 in molarity $= \frac{\text{Normality}}{2} = \frac{36\cdot8}{2} = 18\cdot4$(M)

6. *A laboratory bottle containing conc. H_2SO_4 is labelled as 86% H_2SO_4. Its density is 1·787 g/ml. Calculate the strength of the solution in molarity.*
[W.B.H.S. '79, I.I.T. '79]

Ans : Density of $H_2SO_4 = 1\cdot787$ g/ml (Given)
∴ Weight of 1000 ml $H_2SO_4 = 1\cdot787\times1000 = 1787$ g
100 g of impure acid contain 86 g of pure H_2SO_4
1787 g of impure acid contain $\frac{86\times1787}{100} = 1536\cdot82$ g
or, 1000 ml H_2SO_4 contain 1536·82 g
∴ Molarity of $H_2SO_4 = \frac{1536\cdot82}{98} = 15\cdot68$
∴ The concentration of the commercial $H_2SO_4 = 15\cdot68$ (M)

[F] Calculation of strength of acid or alkali by applying the formula $V_1S_1 = V_2S_2$

7. *25 ml of H_2SO_4 is required to neutralise 20 ml of 1·5 $\left(\frac{N}{10}\right)$ Na_2CO_3 solution.*

Calculate the strength of H_2SO_4 in (i) Normality, (ii) Gram per litre and (iii) Molarity.

Ans : Let the strength of H_2SO_4 be S_1 and applying the formula $V_1S_1 = V_2S_2$

$$25 \times S_1 = 20 \times 1\cdot5\left(\frac{N}{10}\right)$$

$$S_1 = \frac{20 \times 1\cdot5}{25}\left(\frac{N}{10}\right) = 0\cdot12\,(N)$$

Hence strength of $H_2SO_4 = 0\cdot12(N)$ and gram per litre $= 0\cdot12 \times 49 = 5\cdot88$

Strength of H_2SO_4 in molarity $= \frac{0\cdot12}{2} = 0\cdot06\,(M)$

8. *4·9 g of H_2SO_4 are mixed with water and the total volume becomes 500 ml. Calculate the volume of this acid to neutralise 25 ml of 5% Na_2CO_3 solution.*

Ans : 500 ml H_2SO_4 solution contain 4·9 g of H_2SO_4
1000 ml H_2SO_4 solution contain 9·8 g of H_2SO_4

∴ Strength of $H_2SO_4 = \frac{9\cdot8}{49} = 0\cdot2\,(N)$

The strength of 5% Na_2CO_3 in terms of normality $= \frac{5 \times 10}{53}\,(N) = 0\cdot9434\,(N)$

Let the volume of acid $= V_1$

$$V_1 \times 0\cdot2\,(N) = 25 \times 0\cdot9434\,(N)$$

$$V_1 = \frac{25 \times 0\cdot9434}{0\cdot2} = 117\cdot9\text{ ml}$$

∴ The volume of the acid = 117·9 ml

9. *The density of a sample of $H_2SO_4 = 1\cdot8$ g/ml. It contains 40% H_2SO_4. 10 ml sample of a Na_2CO_3 solution contains 0·53 g. What volume of H_2SO_4 is required to neutralise 100 ml of this Na_2CO_3 solution ?*

Ans : 1000 ml H_2SO_4 contain $1\cdot8 \times 1000 = 1800$ g H_2SO_4

Again 1800 g H_2SO_4 contain $\frac{40 \times 1800}{100} = 720$ g of pure H_2SO_4

∴ Strength of $H_2SO_4 = \frac{720}{49} = 14\cdot69\,(N)$

Again, 10 ml of Na_2CO_3 contain 0·53 g of Na_2CO_3
1000 ml of Na_2CO_3 contain 53 g of Na_2CO_3

∴ Strength of $Na_2CO_3 = \frac{53}{53} = 1\cdot0\,(N)$

$$V_1 \times 14\cdot69\,(N) = 100 \times 1\,(N)$$

$$V_1 = \frac{100 \times 1}{14\cdot69} = 6\cdot8\text{ ml.}$$

10. *The molecular weight of a dibasic acid is 126. 1·42 g of this acid is dissolved in 250 ml solution. 25 ml of a NaOH solution are required to neutralise 22·5 ml of this acid solution. Again 10 ml of a solution of H_2SO_4 can neutralise 12 ml of this NaOH solution. Calculate the strength of H_2SO_4 in normality.*

Ans : 1000 ml of acid solution contain $\frac{1\cdot42 \times 1000}{250} = 5\cdot68$ g of the dibasic acid.

Eq. wt. of the acid $= \frac{126}{2} = 63$

∴ Strength of the acid $= \frac{5\cdot68}{63} = 0\cdot09\,(N)$

Let the strength of NaOH be S_2 (N)

$$22\cdot5 \times 0\cdot09\,(N) = 25 \times S_2$$

$$S_2 = \frac{22\cdot5 \times 0\cdot09}{25}\ (\mathrm{N}) = 0\cdot08\ (\mathrm{N})$$

$\therefore$ Strength of NaOH solution = 0·08 (N)
Again, let the strength of H_2SO_4 be S_1 (N)

$\therefore\ 10 \times S_1 = 12 \times 0\cdot08$ (N)

$$S_1 = \frac{12 \times 0\cdot08}{10}\ (\mathrm{N}) = 0\cdot096\ (\mathrm{N})$$

$\therefore$ The strength of H_2SO_4 = 0·096 (N)

11. *A sample of Na_2CO_3 contains Na_2SO_4 as impurity. 1·25 g of this sample is dissolved in water and the volume is made up to 250 ml. 25 ml of this solution can neutralise 20 ml of $\left(\frac{N}{10}\right)$ H_2SO_4. Calculate the percentage of Na_2SO_4 in the sample.*

Ans : 1000 ml of Na_2CO_3 solution contains $\frac{1\cdot25 \times 1000}{250} = 5\cdot0$ g
Let the strength of this solution be S_1 (N)

$$25 \times S_1 = 20 \times \frac{\mathrm{N}}{10}$$

or, $S_1 = 0\cdot08$ (N)
$\therefore$ Weight of Na_2CO_3 in g per litre = $0\cdot08 \times 53 = 4\cdot24$ g
$\therefore$ In 5 g Na_2CO_3 in 1000 ml solution, 4·24 g of pure Na_2CO_3 is actually present.
$\therefore$ Weight of $Na_2SO_4 = 5 - 4\cdot24 = 0\cdot76$ g
$\therefore$ 5 g sample contain 0·76 g of Na_2SO_4

100 g sample contain $\frac{0\cdot76 \times 100}{5} = 15\cdot2$ g of Na_2SO_4

$\therefore$ % of $Na_2SO_4 = 15\cdot2\%$

12. *0·12 g of a bivalent metal is dissolved in 50 ml of N/2 HCl. The volume is made up to 100 ml with water 20 ml of this solution neutralise 30 ml of $\left(\frac{N}{10}\right)$ NaOH. Calculate the equivalent weight and atomic weight of the metal.*

Ans : 50 ml of (N/2) HCl $\equiv$ 50 × 1/2 ml of (N) HCl $\equiv$ 25 ml of (N) HCl
Let S_1 be the strength of the acid after the reaction with metal.

or, $20 \times S_1 = 30 \times \frac{\mathrm{N}}{10}$

or, $S_1 = \frac{30}{20 \times 10}\ (\mathrm{N}) = \frac{3}{20}\ (\mathrm{N})$

or, the strength of 100 ml HCl = $\frac{3}{20}$ (N)

Now 100 ml of $\frac{3}{20}$ (N) HCl $\equiv \left(100 \times \frac{3}{20}\right)$ ml of (N) HCl $\equiv$ 15 ml of (N) HCl

$\therefore$ 15 ml of (N) HCl is left after the reaction with the metal.
This volume of HCl is neutralised by NaOH.
$\therefore$ Vol of HCl that reacts with the metal = (25 − 15) = 10 ml (N) HCl
or, 10 ml of (N) HCl $\equiv$ 0·12 g of the metal

1000 ml of (N) HCl $\equiv \frac{0\cdot12 \times 1000}{10} = 12$ g metal

$\therefore$ Eq. wt. of the metal = 12
At. wt. of the metal = 12 × 2 = 24

13. *A solution of H_2SO_4 of density 1·84 g/ml contains 98% pure acid. What volume of this acid is required to prepare 200 ml of 0·5 (N) H_2SO_4 ?* **[I.I.T. 1976]**

Ans : Weight of 1000 ml of the acid = 1·84 × 1000 = 1840 g

Again 1840 g of this acid contains $\frac{98 \times 1840}{100} = 1803{\cdot}2$ g

$\therefore$ The strength of the acid $= \frac{1803{\cdot}2}{49} = 36{\cdot}8$ (N)

Let V_1 ml of this acid is required

$$V_1 \times 36{\cdot}8\,(\mathrm{N}) = 200 \times 0{\cdot}5\,(\mathrm{N})$$

$$V_1 = \frac{200 \times 0{\cdot}5}{36{\cdot}8} = 2{\cdot}72\text{ ml}$$

$\therefore$ The required volume of $H_2SO_4 = 2{\cdot}72$ ml.

[G] To find the volume of water for the reduction of the concentration of a solution.

14. (i) *What volume of water is required to reduce 3 ml of 12 (N) H_2SO_4 into $\left(\frac{N}{10}\right)$?*

(ii) *20 ml of H_2SO_4 neutralise 30 ml of 5% NaOH solution. How much water is to be added to this 25 ml H_2SO_4 solution to make it exactly $\left(\frac{N}{10}\right)$?*

(iii) *You are given 25 ml of 1·18 $\left(\frac{N}{10}\right)$ Na_2CO_3. How can you prepare exactly $\left(\frac{N}{10}\right)$ Na_2CO_3 solution ?*

Ans : (i) Let the volume of acid required be V ml

$$\therefore\ V \times \frac{\mathrm{N}}{10} = 3 \times 12\,(\mathrm{N})$$

$$\text{or, } V = 3 \times 10 \times 12 = 360\text{ ml}$$

Given volume of 12 (N) $H_2SO_4 = 3$ ml

$\therefore$ The required volume of water $= (360 - 3) = 357$ ml.

or, 357 ml water + 3 ml 12 (N) H_2SO_4 solution will be exactly $\left(\frac{\mathrm{N}}{10}\right)$ H_2SO_4 solution.

(ii) Strength of 5% NaOH $= \frac{10 \times 5}{40}$ (N) $= 1{\cdot}25$ (N)

Let the strength of H_2SO_4 be S_1 (N)

$$20 \times S_1 = 30 \times 1{\cdot}25\,(\mathrm{N})$$

$$\text{or, } S_1 = \frac{30 \times 1{\cdot}25}{20}\,(\mathrm{N})$$

$$\text{or, } S_1 = 1{\cdot}875\,(\mathrm{N})$$

Let the volume of decinormal acid be V ml

$$V \times \frac{\mathrm{N}}{10} = 25 \times 1{\cdot}875$$

$$V = 10 \times 25 \times 1{\cdot}875 = 468{\cdot}75\text{ ml.}$$

Hence volume of water required $= 468{\cdot}75 - 25 = 443{\cdot}75$ ml

So, when 443·75 ml of water is added to 25 ml of H_2SO_4 the strength of the later becomes exactly decinormal.

(iii) 25 ml of 1·18 $\left(\frac{\mathrm{N}}{10}\right)$ Na_2CO_3 solution

$\equiv 25 \times 1{\cdot}18$ ml of $\left(\frac{\mathrm{N}}{10}\right)$ Na_2CO_3 solution

$\equiv 29{\cdot}5$ ml $\left(\frac{\mathrm{N}}{10}\right)$ Na_2CO_3 solution

Hence to make it exactly $\left(\frac{\mathrm{N}}{10}\right)$ $Na_2CO_3 = 29{\cdot}5 - 25 = 4{\cdot}5$ ml of water to be added.

15. *22·5 ml NaOH neutralises 25 ml $\left(\frac{N}{10}\right)$ HCl. How much water is to be added to 1 litre of this NaOH solution to make it exactly $\left(\frac{N}{10}\right)$?*

Ans : Let the strength of NaOH be S_1

$$22{\cdot}5 \times S_1 = 25 \times \left(\frac{N}{10}\right)$$

or, $S_1 = 0{\cdot}1111{\cdot}(N)$

Let after addition of water to 1000 ml 0·1111 (N) NaOH the total volume be V ml and the strength becomes N/10.

$\therefore\ 1000 \times 0{\cdot}1111\,(N) = V \times \frac{N}{10}$

or, $V = 1111$ ml

$\therefore$ Vol of water to be added to 1000 ml 0·1111 (N) NaOH = 1111 − 1000 = 111 ml

$\therefore$ The strength of the required solution will be exactly N/10

16. (i) *500 ml of water is added to 100 ml 0·60 (M) of a solution. Calculate the strength of the solution in molarity.*

(ii) *How many moles of water is present in 1 litre of water ?* [*J.E.E. 1983*]

Ans : (i) Let the strength of the solution be S_1

Volume of the solution = 100 + 500 = 600 ml

$100 \times 0{\cdot}6\,M = 600 \times S_1$

$$S_1 = \frac{100 \times 0{\cdot}6}{600} = 0{\cdot}1\,(M)$$

(ii) Since density of water is 1 g/ml, the weight of 1000 ml water = 1000 g

Molecular weight of water is = 18

$\therefore$ Number of moles $= \frac{1000}{18} = 55{\cdot}55$ mole.

17. *What is the molarity of 13% H_2SO_4 ? The density of this acid is 1·02 g/ml. Find the volume of water to be added to 100 ml of this acid to make the solution 1·5 (N)* [*I.I.T. 1978*]

Ans : Weight of 1000 ml solution = 1·02 × 1000 = 1020 g

Amount of H_2SO_4 in 1020 g of acid solution $= \frac{13 \times 1020}{100} = 132{\cdot}6$ g

$\therefore$ Molarity of $H_2SO_4 = \frac{132{\cdot}6}{98} = 1{\cdot}35\,(M)$

$\therefore$ Normality of $H_2SO_4 = 1{\cdot}35 \times 2 = 2{\cdot}7\,(N)$

Let V be the volume of the solution whose strength is 1·5 (N)

$\therefore\ 100 \times 2{\cdot}7\,(N) = V \times 1{\cdot}5\,(N)$

or, $V = 180$ ml

$\therefore$ Vol of water to be added to 100 ml H_2SO_4 of 2·7 (N) = (180 − 100) = 80 ml.

[H] Strength of resulting solution on mixing two acids or two alkalis separately of known strength and volume, or on mixing one acid with another alkali of known strength and volume.

18. *30 ml of 0·01 (N) Na_2CO_3 solution is mixed with 40 ml of $\left(\frac{N}{5}\right)$ KOH and 20 ml of $\left(\frac{N}{10}\right)$ NaOH solution. What is the strength of the resulting solution ?*

Ans : 30 ml of 0·01 (N) $Na_2CO_3 \equiv (30 \times 0{\cdot}01)$ ml of 1 (N) Na_2CO_3

$\equiv 0{\cdot}3$ ml of 1 (N) Na_2CO_3

40 ml of $\left(\frac{N}{5}\right)$KOH $\equiv \left(40 \times \frac{1}{5}\right)$ ml of 1 (N) KOH $\equiv$ 8 ml of 1 (N) KOH

20 ml of $\left(\frac{N}{10}\right)$ NaOH $\equiv \left(20 \times \frac{1}{10}\right)$ ml of 1 (N) NaOH $\equiv$ 2 ml of 1 (N) NaOH

$\therefore$ Total volume = 0·3 + 8 + 2 = 10·3 ml of 1 (N) alkali

Total volume of the mixed solution = 30 + 40 + 20 = 90 ml

Let S_1 be the strength of the mixed solution

$$90 \times S_1 = 10{\cdot}3 \times 1\,(N)$$

$$S_1 = \frac{10{\cdot}3}{90}\,(N) = 0{\cdot}1144\,(N)$$

19. *50 ml of 1·04* $\left(\frac{N}{10}\right)$ *H_2SO_4 are mixed with 20 ml of* $\left(\frac{N}{5}\right)$ *NaOH, 15 ml of* $\left(\frac{N}{2}\right)$ *HCl and 25 ml of 0·12 (N) KOH. Will the mixed solution be acidic, alkaline or neutral ? If not neutral what will be the strength of the resulting solution ?*

Ans : 50 ml of 1·04$\left(\frac{N}{10}\right)$ $H_2SO_4 \equiv \frac{50 \times 1{\cdot}04}{10}$ ml of (N) H_2SO_4 = 5·2 ml of 1 (N) H_2SO_4

15 ml of$\left(\frac{N}{2}\right)$ HCl $\equiv 15 \times \frac{1}{2}$ ml of (N) HCl $\equiv$ 7·5 ml of 1 (N) HCl

$\therefore$ Total volume of the acid = 50 + 15 = 65 ml

Total volume of the acid expressed in 1 normal = 5·2 + 7·5 = 12·7 ml

Again, 20 ml of $\left(\frac{N}{5}\right)$ NaOH $\equiv \left(20 \times \frac{1}{5}\right)$ ml of 1 (N) NaOH $\equiv$ 4 ml of 1 (N) NaOH

25 ml of 0·12 (N) KOH $\equiv$ (25 × 0·12) ml of 1 (N) KOH = 3 ml of 1 (N) KOH

Total volume of the alkali = 20 + 25 = 45 ml and the volume of the alkali expressed in 1 normal = 4 + 3 = 7 ml.

7 ml of 1 (N) alkali will neutralise 7 ml of 1 (N) acid.

$\therefore$ Excess unneutralised acid = (12·7 − 7) = 5·7 ml of 1 (N)

The resulting solution will be acidic.

The total volume on mixing the four liquids = 50 + 15 + 20 + 25 = 110 ml

Let the strength of the resulting solution be S_1

$$110 \times S_1 = 5{\cdot}7 \times 1\,(N)$$

$$S_1 = \frac{5{\cdot}7}{110}\,(N) = 0{\cdot}0518\,(N)$$

20. *25 ml of 0·5 (N) HCl is mixed with 50 ml of 0·8% NaOH. Will the resulting solution be acidic or alkaline ? Calculate the strength of the solution.*

[*W.B.H.S. 1981*]

Ans : 100 ml of NaOH solution contain 0·8 g of NaOH

1000 ml of NaOH solution contain 8 g of NaOH

$\therefore$ Strength of NaOH = $\frac{8}{40}$ (N) = $\frac{1}{5}$ (N)

50 ml of $\frac{1}{5}$ (N) NaOH $\equiv \left(50 \times \frac{1}{5}\right)$ ml of 1 (N) NaOH = 10 ml of 1 (N) NaOH

25 ml of 0·5 (N) HCl $\equiv$ (25 × 0·5) ml of 1 (N) HCl $\equiv$ 12·5 ml of 1 (N) HCl

10 ml of 1 (N) NaOH neutralise 10 ml of 1 (N) HCl

Hence excess unneutralised acid = (12·5 − 10) = 2·5 ml of 1 (N) acid. The resulting solution is acidic.

The total volume of the resulting solution = 75 ml

Let the strength be S_1

or, $75 \times S_1 = 2{\cdot}5 \times 1\,(N)$

$$S_1 = \frac{2{\cdot}5}{75}\,(N) = 0{\cdot}033\,(N)$$

21. *1 g of pure NaOH is dissolved in water to form 100 ml solution. To it is added 5 ml of (N) H_2SO_4. State whether the resulting solution is acidic or alkaline. Find the strength of the resulting solution.* [*J.E.E. 1980*]

Ans : Strength of NaOH $= \frac{10}{40}$ (N) $= \frac{N}{4}$

100 ml of $\left(\frac{N}{4}\right)$ NaOH solution $\equiv \left(100 \times \frac{1}{4}\right)$ ml of 1 (N) NaOH $\equiv$ 25 ml of 1 (N) NaOH

5 ml of (N) H_2SO_4 can neutralise 5 ml of (N) NaOH. Hence $(25 - 5) = 20$ ml of 1 (N) NaOH will remain unneutralised.

The resulting solution is alkaline.

Let S_1 be the strength of the resulting solution and total volume of the final solution = 105 ml.

$\therefore$ $105 \times S_1 = 20 \times 1$ (N)

$$S_1 = \frac{20}{105}\,(\text{N}) = \frac{4}{21}\,(\text{N}) = 0{\cdot}19\,(\text{N})$$

The strength of the resulting solution is 0·19 (N).

[I] To calculate the total quantity of NH_3 or nitrogen from ammonium salt by decomposing it with strong alkali and back titrating the resulting alkali with known volume standard acid (Kjeldahal's method of estimation of NH_3)

[**Principle of Kjeldahal's method :** This is a very convenient method for the estimation of nitrogen in nitrogeneous organic compounds like fertiliser, proteins etc., and is commonly used in agricultural laboratory. The method consists in converting a known weight of a nitrogenous organic compound into $(NH_4)_2SO_4$ by heating it strongly with conc. H_2SO_4 in presence of $CuSO_4$ catalyst. K_2SO_4 is added to raise the boiling point of H_2SO_4. The operation is done in a long necked flask known as *Kjeldahal's flask*. The contents are next taken in a round bottom flask, to it is added strong NaOH solution. The whole mixture is slowly heated. NH_3 is quantitatively liberated which is absorbed in a known volume of standard acid. The excess acid is back titrated against a standard alkali using phenolphthalein indicator.]

22. *1·524 g of NH_4Cl is dissolved in water. 100 ml of (N/2) KOH is added to it. The mixture is heated till NH_3 is completely liberated from the mixture. The solution is cooled to room temperature and is neutralised by 30·95 ml of 1 (N) H_2SO_4. Calculate the percentage of NH_3 in NH_4Cl.* [*Cal. Univ. 1964*]

Ans :

100 ml of (N/2) KOH $\equiv$ (100×1/2) ml of (N) KOH $\equiv$ 50 ml of (N) KOH

30·95 ml of (N) H_2SO_4 will neutralise 30·95 ml of (N) KOH

$\therefore$ Volume of KOH required to liberate NH_3 from NH_4Cl = (50 − 30·95)

= 19·05 ml of 1(N) KOH

Now 19·05 ml of (N) KOH $\equiv$ 19·05 ml of (N) NH_3

1000 ml of 1(N) NH_3 solution contain 17 g of NH_3

19·05 ml of (I) N NH_3 solution contain $\frac{17 \times 19{\cdot}05}{1000} = 0{\cdot}3238$ g

$\therefore$ % of NH_3 in $NH_4Cl = \frac{0{\cdot}3238 \times 100}{1{\cdot}524} = 21{\cdot}25$

23. *10 ml solution of $(NH_4)_2SO_4$ is boiled with excess of NaOH solution. The NH_3 liberated is absorbed in 50 ml of 0·1 (N) HCl solution. 10 ml of 0·2 (N) NaOH is used to back titrate the excess acid. Find the total quantity of $(NH_4)_2SO_4$ in 1 litre of the solution.* [*I.I.T. 1978)*

Ans : 50 ml of 0·1 (N) HCl $\equiv$ (50 × 0·1) ml of (N) HCl $\equiv$ 5 ml of (N) HCl

10 ml of 0·2 (N) NaOH $\equiv$ (10 × 0·2) ml of (N) NaOH $\equiv$ 2 ml of (N) NaOH

$\equiv$ 2 ml of (N) HCl

$\therefore$ The volume of NaOH that reacts with $(NH_4)_2SO_4$ = (5 − 2) = 3 ml.

or, 3 ml of 1 (N) NaOH $\equiv$ 3 ml of 1 (N) HCl

The equivalent weight of $(NH_4)_2SO_4 = \dfrac{2 \times 14 + 8 + 32 + 64}{2} = 66$

$$1000 \text{ ml of } 1\text{ (N) HCl} \equiv 66 \text{ g of } (NH_4)_2SO_4$$

$$3 \text{ ml of } 1\text{ (N) HCl} \equiv \frac{66 \times 3}{1000} = 0{\cdot}198 \text{ g of } (NH_4)_2SO_4$$

Hence, 10 ml of $(NH_4)_2SO_4$ solution contain 0·198 g of $(NH_4)_2SO_4$

$$1000 \text{ ml of } (NH_4)_2SO_4 \text{ solution contain } \frac{0{\cdot}198 \times 1000}{10} = 19{\cdot}8 \text{ g of } (NH_4)_2SO_4$$

24. *50 ml of (N) NaOH solution is added to 2 g of a mixture of NH_4Cl and NaCl. The resulting solution is boiled till the red litmus paper does not show change of colour held in the vapour. It is cooled and neutralised with 20 ml of (N) H_2SO_4. Calculate the percentage of NH_4Cl in the mixture.* [*W.B.H.S. 1979*]

Ans : $\underset{53\cdot5\text{ g}}{NH_4Cl} + \underset{40\text{ g}}{NaOH} = NaCl + NH_3 + H_2O$

After the reaction is over, the solution contains some excess NaOH solution which is neutralised by 20 ml of (N) H_2SO_4

20 ml (N) $H_2SO_4 \equiv$ 20 ml (N) NaOH

Volume of NaOH required to liberate NH_3 from NH_4Cl = (50 − 20) = 30 ml

Now, 1000 ml of (N) NaOH contain 40 g of NaOH

$$30 \text{ ml of (N) NaOH contain } \frac{40 \times 30}{1000} = 1{\cdot}2 \text{ g}$$

Again, 40 g NaOH react with 53·5 g of NH_4Cl

$$1{\cdot}2 \text{ g NaOH react with } \frac{53{\cdot}5 \times 1{\cdot}2}{40} = 1{\cdot}605 \text{ g of } NH_4Cl$$

$$\therefore \ \% \text{ of } NH_4Cl = \frac{1{\cdot}605 \times 100}{2} = 80{\cdot}25\%$$

[J] Mixing of two solutions of known strength in definite proportion to obtain resultant solution of known strength.

25. *When V_2 volume of water is added to V_1 volume of solution of M_1 molar strength, the resulting solution becomes M_2 molar. Calculate the volume of water added.* [*I.I.T. 1977*]

Ans : The total volume = $(V_1 + V_2)$. Its strength is M_2

$V_1 \times M_1 = (V_1 + V_2)M_2$

or, $V_1 \times M_1 = V_1M_2 + V_2M_2$

or, $V_2M_2 = V_1M_1 - V_1M_2$

or, $V_2M_2 = V_1(M_1 - M_2)$

or, $V_2 = \dfrac{V_1(M_1 - M_2)}{M_2}$

26. *Calculate the ratio in volume of two solutions of strength 0·08 (N) H_2SO_4 and 0·14 (N) H_2SO_4 when mixed together to give a resulting solution of exactly $\left(\frac{N}{10}\right)$ H_2SO_4.*

Ans : Let *x* ml of 0·08 (N) H_2SO_4 when mixed with *y* ml of 0·14 (N) H_2SO_4, the strength of the resulting solution is exactly $\left(\frac{N}{10}\right)$.

x ml of 0·08 (N) $H_2SO_4 \equiv (x \times 0{\cdot}08)$ ml of (N) H_2SO_4

y ml of 0·14 (N) $H_2SO_4 \equiv (y \times 0{\cdot}14)$ ml of (N) H_2SO_4

or, the mixture contains $(x \times 0{\cdot}08 + y \times 0{\cdot}14)$ ml of (N) H_2SO_4

The total volume of the resulting solution = $(x + y)$ ml

$$\therefore \ (x \times 0{\cdot}08 + y \times 0{\cdot}14) \text{ ml of (N) } H_2SO_4 = (x + y) \text{ ml} \left(\frac{N}{10}\right) H_2SO_4$$

$$(0{\cdot}08x + 0{\cdot}14y) \times \mathrm{N} = (x + y) \times \frac{\mathrm{N}}{10}$$

$$0{\cdot}08x + 0{\cdot}14y = \frac{x + y}{10}$$

or, $0{\cdot}8x + 1{\cdot}4y = x + y$
or, $x - 0{\cdot}8x = 1{\cdot}4y - y$
or, $0{\cdot}2x = 0{\cdot}4y$
or, $\frac{x}{y} = \frac{4}{2} = \frac{2}{1}$

or, when 2 volumes of 0·08 (N) H_2SO_4 is mixed with 1 volume of 0·14 (N) H_2SO_4, the resulting solution becomes exactly $\left(\frac{\mathrm{N}}{10}\right)$.

27. *15 ml of 0·08 (N) KOH and 35 ml of KOH of same concentration are required to neutralise 15 ml of an acid A_1 and 20 ml of an acid A_2 respectively. In what proportion by volume of the two acids should be mixed to obtain a resulting solution of strength exactly 0·1 (N) ?*

Ans : Since 15 ml of 0·08 (N) KOH is required to neutralise 15 ml of the acid A_1, the strength of A_1 is 0·08 (N)

Again, 35 ml of 0·08 (N) KOH is required to neutralise 20 ml of the acid A_2

$\therefore$ Strength of the acid $A_2 = \frac{35 \times 0{\cdot}08}{20}$ (N) = 0·14 (N)

Let the volumes the acids A_1 and A_2 be V_1 and V_2 ml respectively.
$\therefore$ Total volume of the acids = $(V_1 + V_2)$ ml
V_1 ml of 0·08 (N) acid $A_1 = (V_1 \times 0{\cdot}08)$ ml of (N) acid A_1
V_2 ml of 0·14 (N) acid $A_2 = (V_2 \times 0{\cdot}14)$ ml of (N) acid A_2
$\therefore$ Mixed acid = $(0{\cdot}08V_1 + 0{\cdot}14V_2)$ ml of (N) acid
According to the problem,
$(V_1 + V_2)$ of 0·1 (N) = $(0{\cdot}08V_1 + 0{\cdot}14V_2)$ of (N)
or, $\frac{V_1 + V_2}{10} = 0{\cdot}08V_1 + 0{\cdot}14V_2$
or, $V_1 + V_2 = 0{\cdot}8V_1 + 1{\cdot}4V_2$
or, $\frac{V_1}{V_2} = \frac{2}{1}$

or, 2 volumes of A_1 when mixed with 1 volume of A_2 the resulting solution will be exactly 0·1 (N).

28. *You are given an acid of strength 0·5 (N) and an alkali of strength 0·6 (N). In what proportion by volume the two solutions should be mixed so that the resulting solution will be (i) Neutral, (ii) 0·05 (N) Acidic and (iii) 0·08 (N) Alkaline ?*

Ans : Let x ml of 0·5 (N) acid be mixed with y ml of 0·6 (N) alkali.
$\therefore$ Total volume of the solution = $(x + y)$ ml
Now x ml of 0·5 (N) acid = $(x \times 0{\cdot}5)$ ml of (N) acid = $0{\cdot}5x$ ml of (N) acid
Again y ml of 0·6 (N) alkali = $(y \times 0{\cdot}6)$ ml of (N) alkali = $0{\cdot}6y$ ml of (N) alkali

(i) The resulting solution will be neutral when $0{\cdot}5x$ ml of (N) acid neutralises exactly $0{\cdot}6y$ ml of (N) alkali.
or, $0{\cdot}5x = 0{\cdot}6y$
or, $\frac{x}{y} = \frac{0{\cdot}6}{0{\cdot}5} = \frac{6}{5}$

Hence when the ratio of the volume of the acid and the alkali = 6 : 5, the resulting solution will be exactly neutral.

(ii) If the resulting solution be 0·05 (N) acidic then $0\cdot5x$ ml > $0\cdot6y$ ml
Under this condition $0\cdot6y$ ml of (N) alkali will neutralise $0\cdot6y$ ml of (N) acid
∴ Excess acid = $(0\cdot5x - 0\cdot6y)$ ml (N) acid
or, According to the condition,
$(x + v) \times 0\cdot05\ (N) = (0\cdot5x - 0\cdot6y) \times (N)$
or, $0\cdot05x + 0\cdot05y = 0\cdot5x - 0\cdot6y$
or, $0\cdot45x = 0\cdot65y$
or, $\frac{x}{y} = \frac{0\cdot65}{0\cdot45} = \frac{13}{9}$

If the volume ratio of the acid and alkali be 13 : 9 then the resulting solution will be acidic and its strength will be 0·05 (N).

(iii) The condition for the resulting solution being 0·08 (N) alkaline is $0\cdot6y$ ml > $0\cdot5x$ ml. Under this condition $0\cdot5x$ ml acid will neutralise $0\cdot5x$ ml of alkali.
∴ Excess alkali = $(0\cdot6y - 0\cdot5x)$ ml of (N) alkali
According the condition of the problem,
$(x + y) \times 0\cdot08\ (N) = (0\cdot6y - 0\cdot5x) \times 1\ (N)$
or, $0\cdot08x + 0\cdot08y = 0\cdot6y - 0\cdot5x$
or, $0\cdot58x = 0\cdot52y$
or, $\frac{x}{y} = \frac{0\cdot52}{0\cdot58} = \frac{26}{29}$

Hence when the volume ratio of acid and alkali be 26 : 29 the resulting solution will be alkaline and its strength will be 0·08 (N).

[K] Miscellaneous problems.

29. *At N.T.P. when 600 ml of HCl gas is passed into NaOH solution, the resulting solution still remains alkaline. When 50 ml of 1·2 (N) H_2SO_4 is added to the solution it becomes neutral. Calculate the weight of NaOH in the solution.*

Ans : At N.T.P. 22400 ml of HCl contain 36·5 g of HCl

At N.T.P. 600 ml of HCl contain $\frac{36\cdot5 \times 600}{22400} = 9\cdot777$ g of HCl.

9·777 g HCl react with $\frac{40 \times 9\cdot777}{36\cdot5} = 10\cdot7145$ g of NaOH

Now 50 ml of 1·2 (N) H_2SO_4 = (50 × 1·2) ml of (N) H_2SO_4 = 60 ml of (N) H_2SO_4
1000 ml of (N) H_2SO_4 contain 49 g of H_2SO_4

60 ml of (N) H_2SO_4 contain $\frac{49 \times 60}{1000} = 2\cdot94$ g of H_2SO_4

Again 49 g of H_2SO_4 neutralise 40 g of NaOH

2·94 g of H_2SO_4 neutralise $\frac{40 \times 2\cdot94}{49} = 2\cdot4$ g of NaOH

Hence total weight of alkali neutralised by acid = (10·7145 + 2·4) = 13·1145 g
∴ Weight of NaOH dissolved in the solution = 13·1145 g.

30. *0·75 g of a bivalent metal is dissolved in 350 ml of $\left(\frac{N}{10}\right)$ H_2SO_4. The excess acid is neutralised by 40 ml of $\left(\frac{N}{5}\right)$ Na_2CO_3 solution. Calculate the atomic weight of the metal.*

Ans. 40 ml of $\left(\frac{N}{5}\right)$ Na_2CO_3 = $\left(40 \times \frac{1}{5}\right)$ ml of (N) Na_2CO_3 = 8 ml of (N) Na_2CO_3

8 ml of (N) $Na_2CO_3 \equiv$ 8 ml of (N) $H_2SO_4 \equiv$ 80 ml of $\left(\frac{N}{10}\right)$ H_2SO_4

∴ Volume of Acid that reacts with the metal

$= (350 - 80) = 270$ ml of $\left(\frac{N}{10}\right)$ $H_2SO_4 = 27$ ml of (N) H_2SO_4

Now, 27 ml of (N) H_2SO_4 dissolve 0·75 g of metal

1000 ml of (N) H_2SO_4 dissolve $\frac{0{\cdot}75 \times 1000}{27} = 27{\cdot}8$ g of metal

$\therefore$ Equivalent weight of the metal = 27·8

Hence the atomic weight = 27·8 × 2 = 55·6

31. *0·01 gram-atom of zinc metal is completely dissolved in 90·5 ml of dilute H_2SO_4 solution. The resulting solution is neutralised by 17·5 ml of 0·15 (N) NaOH solution. Find the strength of the acid in normality and the weight of $ZnSO_4$ formed. (Zn = 65·38, S = 32, O = 16)* [*J.E.E. 1974*]

Ans : $\underset{\text{1 g atom}}{Zn} + \underset{\text{98 g}}{H_2SO_4} = \underset{\text{161·38 g}}{ZnSO_4} + H_2$

1 gram-atom Zn reacts with 98 g of H_2SO_4

0·01 gram-atom Zn reacts with 98 × 0·01 = 0·98 g of H_2SO_4

Again 17·5 ml of 0·15 (N) NaOH $\equiv$ (17·5 × 0·15) ml of 1 (N) NaOH

$\equiv$ 2·625 ml of 1 (N) NaOH

$\equiv$ 2·625 ml of 1 (N) H_2SO_4

2·625 ml of 1 (N) H_2SO_4 contain $\frac{49 \times 2{\cdot}625}{1000} = 0{\cdot}1286$ g of H_2SO_4

$\therefore$ Total $H_2SO_4 = 0{\cdot}98 + 0{\cdot}1286 = 1{\cdot}1086$ g

$\therefore$ 90·5 ml of H_2SO_4 contain 1·1086 g of H_2SO_4

1000 ml of H_2SO_4 contain $\frac{1{\cdot}1086 \times 1000}{90{\cdot}5} = 12{\cdot}249$ g of H_2SO_4

$\therefore$ Strength of $H_2SO_4 = \frac{12{\cdot}249}{49}$ (N) = 0·2499 (N)

Again 1 gram-atom Zn yields 161·38 g of $ZnSO_4$

0·01 gram-atom Zn yields 161·38 × 0·01 = 1·6138 g.

Hence the strength of H_2SO_4 = 0·2499 (N) and the weight of $ZnSO_4$ = 1·6138 g.

32. *2 g of an impure blue vitriol were dissolved in water and boiled with 25 ml of (N) NaOH solution. The resulting black precipited was filtered and washed. The filtrate and washing required 15 ml of (N) H_2SO_4 for neutralisation. Calculate the percentage purity of the salt. (Cu = 63·5)* [*J.E.E. 1985*]

Ans. $\underset{\text{1 mole}}{CuSO_4} + \underset{\substack{\text{2 mole or}\\ \text{2000 ml of 1(N)}}}{2NaOH} = \underset{\text{black}}{CuO\downarrow} + Na_2SO_4 + H_2O$

The volume of NaOH solution that reacts with 2 g of blue vitriol = (25 − 15) = 10 ml of 1 (N) NaOH

2000 ml of 1 (N) NaOH $\equiv$ 1 mole of $CuSO_4 \equiv$ 1 mole of pure blue vitriol

$\equiv$ 249·5 g of pure blue vitriol

10 ml of 1 (N) NaOH $\equiv \frac{249{\cdot}5 \times 10}{2000} = 1{\cdot}2475$ g of pure blue vitriol

2 g of impure sample contain 1·2475 g pure blue vitriol

100 g of impure sample contain $\frac{1{\cdot}2475 \times 100}{2} = 62{\cdot}375$ g

or, the purity of blue vitriol = 62·375%

33. *The lime obtained on heating 1 g of $CaCO_3$ is dissolved in water to make 1 litre of solution. What is the normality of the solution.* [*W.B.H.S. 1981*]

Ans : $\underset{\text{100 g}}{CaCO_3} = \underset{\text{56 g}}{CaO} + CO_2$

100 g of $CaCO_3$ yield 56 g of CaO

1 g of $CaCO_3$ yields 0·56 g of CaO

The equivalent weight of CaO $= \frac{40+16}{2} = 28$

Since 1 litre of the solution contain 0·56 g of CaO

$\therefore$ The strength of the solution $\frac{0\cdot56}{28} = 0\cdot02$ (N)

34. *1·0 g of a mixture of Na_2CO_3 and $NaHCO_3$ is dissolved in water to make 250 ml solution. 25 ml of the solution requires 15 ml of 0·1 (N) HCl for neutralisation. Calculate the percentage of $NaHCO_3$ in the mixture.*

Ans : Let the weight of $NaHCO_3$ be x g

$\therefore$ Weight of $Na_2CO_3 = (1-x)$ g

25 ml of the solution $\equiv$ 15 ml of 0·1(N) HCl

or, 250 ml of the solution $\equiv$ 150 ml of 0·1(N) HCl $\equiv$ 15 ml of (N) HCl

15 ml of (N) HCl contains $\frac{15 \times 36\cdot5}{1000} = 0\cdot5475$ g of HCl

$$\underset{84\,g}{NaHCO_3} + \underset{36\cdot5\,g}{HCl} = NaCl + CO_2 + H_2O$$

84 g of $NaHCO_3$ react with 36·5 g of HCl

x g of $NaHCO_3$ react with $\frac{36\cdot5x}{84}$ g of HCl

Again $\underset{106\,g}{Na_2CO_3} + \underset{2\times36\cdot5\,g}{2HCl} = 2NaCl + CO_2 + H_2O$

or, $(1-x)$ g of Na_2CO_3 combine with $\frac{2\times36\cdot5\times(1-x)}{106}$ g of HCl

Total weight of HCl that neutralise both $NaHCO_3$ and Na_2CO_3

$$= \frac{36\cdot5x}{84} + \frac{73(1-x)}{106}$$

According to the condition of the problem,—

$$\frac{36\cdot5x}{84} + \frac{73(1-x)}{106} = 0\cdot5475$$

$x = 0\cdot5555$ g

$\therefore$ % of $NaHCO_3 = 55\cdot55\%$

35. *Calculate the (i) molality and (ii) molality of a H_2SO_4 solution of specific gravity 1·198 containing 27% H_2SO_4 by weight.* [*B.I.T. Mesra—1989*]

Ans : (i) Volume of 100 g of H_2SO_4 containing 27% purity $= \frac{100}{1\cdot198}$ ml

or, $\frac{100}{1\cdot198}$ ml of H_2SO_4 solution contain 27 g of pure H_2SO_4

1000 ml of H_2SO_4 solution contain $\frac{27\times1\cdot198\times1000}{100} = 27\times11\cdot98$ g

$\therefore$ Strength of molarity $= \frac{27\times11\cdot98}{98}$ (M) $= 3\cdot3$ (M)

Hence the strength of $H_2SO_4 = 3\cdot3$ (M).

(ii) 100 g of the solution contains 27 g of H_2SO_4

$\therefore$ Weight of solvent in 100 g solution $= 100 - 27 = 73$ g

or, 73 g of the solvent contain 27 g of H_2SO_4

1000 g of the solvent contain $\frac{27\times1000}{73}$ g of H_2SO_4

$\therefore$ The strength in molality $= \frac{27\times1000}{73\times98} = 3\cdot77$ (m)

36. *1·0 g of a mixture of dry Na_2CO_3 and K_2CO_3 is dissolved in water and the volume is made up to 250 ml. 25 ml of the solution is neutralised by 20 ml of HCl solution. 16·24 ml of 0·1 (N) $AgNO_3$ solution is required to precipitate the neutral solution. Calculate (i) the percentage of K_2CO_3 in the mixture and (ii) strength of HCl in g per litre.* *[I.I.T. 1976]*

Ans : 20 ml of HCl solution ≡ 16·24 ml of 0·1 (N) $AgNO_3$ solution
≡ 16·24 ml of 0·1 (N) HCl solution

$$\therefore \text{ Strength of HCl solution} = \frac{16{\cdot}24 \times 0{\cdot}1\,(N)}{20} = 0{\cdot}0812\,(N)$$

Again 25 ml of mixture of alkali solution = 16·24 ml of 0·1 (N) HCl solution

$$\text{or, 250 ml of mixture of alkali solution} \equiv \frac{16{\cdot}24 \times 0{\cdot}1\,(N) \times 250}{25}$$

≡ 16·24 ml of 1 (N) HCl solution

Equivalent weight of $K_2CO_3 = 69$
Equivalent weight of $Na_2CO_3 = 53$
Let the weight of K_2CO_3 in the mixture be x g
∴ Weight of Na_2CO_3 in the mixture $= (1{\cdot}0 - x)$ g
69 g of K_2CO_3 ≡ 1000 ml (N) HCl

$$x \text{ g of } K_2CO_3 \equiv \frac{1000x}{69} \text{ ml of (N) HCl}$$

Again 53 g of Na_2CO_3 ≡ 1000 ml (N) HCl

$$(1{\cdot}0 - x) \text{ g of } Na_2CO_3 \equiv \frac{1000(1-x)}{53} \text{ ml (N) HCl}$$

According to the problem —

$$\frac{1000x}{69} + \frac{1000(1-x)}{53} = 16{\cdot}24$$

$x = 0{\cdot}6006$ g
Hence weight of $K_2CO_3 = 0{\cdot}6006$ g
or, % $K_2CO_3 = 0{\cdot}6006 \times 100 = 60{\cdot}06\%$
Strength of HCl $= 0{\cdot}0812 \times 36{\cdot}5 = 2{\cdot}9638$ gram per litre.

37. *16 ml of N/8 NaOH neutralise 10 ml of a mixture of solution containing H_2SO_4 and HCl. When $BaCl_2$ solution is added to 20 ml of the mixture, 0·3591 g of $BaSO_4$ is precipitated out. Calculate the amount of HCl in 1 litre of the solution.* *[J.E.E. 1976]*

Ans : $BaCl_2 + \underset{98\,g}{H_2SO_4} = \underset{233{\cdot}36\,g}{BaSO_4} + 2HCl$

233·36 g of $BaSO_4$ are formed from 98 g of H_2SO_4

$$0{\cdot}3591 \text{ g of } BaSO_4 \text{ are formed from } \frac{98 \times 0{\cdot}3591}{233{\cdot}36} = 0{\cdot}1508 \text{ g}$$

Hence 20 ml of the mixture contain 0·1508 g of H_2SO_4

$$\text{or, 10 ml of the mixture contain } \frac{0{\cdot}1508}{2} = 0{\cdot}0754 \text{ g of } H_2SO_4$$

$$16 \text{ ml of } \left(\frac{N}{8}\right) \text{ NaOH contain} = \frac{40 \times 16}{1000 \times 8} = 0{\cdot}08 \text{ g of NaOH}$$

$\underset{80\,g}{2NaOH} + \underset{98\,g}{H_2SO_4} = Na_2SO_4 + H_2O$

98 g of H_2SO_4 react with 80 g of NaOH

$$0{\cdot}0754 \text{ g of } H_2SO_4 \text{ reacts with } \frac{80 \times 0{\cdot}0754}{98} = 0{\cdot}0616 \text{ g of NaOH.}$$

∴ Weight of NaOH that combines with HCl $= (0{\cdot}08 - 0{\cdot}0616) = 0{\cdot}0184$ g

$\underset{40\,g}{NaOH} + \underset{36{\cdot}5\,g}{HCl} = NaCl + H_2O$

0·0184 g of NaOH react with $\frac{36\cdot5 \times 0\cdot0184}{40} = 0\cdot01679$ g of HCl

or, 10 ml of the mixture contains 0·01679 g of HCl
1000 ml of the mixture contains 1·679 g of HCl
Hence the amount of HCl = 1·679 g/litre.

38. *Calculate the volume of (N) HCl that react with a mixture of 1 g containing equimolar quantity of Na_2CO_3 and $NaHCO_3$* [*I.I.T. 1971*]

Ans : Let the mixture contains x moles of Na_2CO_3 and x moles of $NaHCO_3$

$\therefore$ Weight of $Na_2CO_3 = 106x$ g and weight of $NaHCO_3 = 84x$ g

Given $106x + 84x = 1$

$190x = 1$

or, $x = \frac{1}{190}$

$\therefore$ Weight of $Na_2CO_3 = \frac{1}{190} \times 106 = \frac{106}{190}$ g

Weight of $NaHCO_3 = \frac{1}{190} \times 84 = \frac{84}{190}$ g

53 g of $Na_2CO_3 \equiv$ 1000 ml of (N) HCl

$\frac{106}{190}$ g of $Na_2CO_3 \equiv \left(\frac{1000}{53} \times \frac{106}{190}\right)$ ml of (N) HCl

$\equiv$ 10·526 ml of (N) HCl

Similarly,

84 g of $NaHCO_3 \equiv$ 1000 ml of (N) HCl

$\frac{84}{190}$ g of $NaHCO_3 \equiv \left(\frac{1000}{84} \times \frac{84}{190}\right)$ ml of (N) HCl $\equiv$ 5·263 ml of (N) HCl

Hence, total volume of HCl = 10·526 + 5·263 = 15·789 ml.

39. *1·00 g of a mixture consisting of equal number of moles of carbonates of two alkali metals, required 44·4 ml of 0·500 (N) HCl for complete neutralisation. If the atomic weight of one of the metals is 7·00 find the atomic weight of the other metal. What will be the total amount of sulphate formed on quantitative conversion of 1·00 g of the mixture into sulphates ?* [*I.I.T. 1972*]

Ans : 44·4 ml of 0·5 (N) HCl $\equiv$ (44·4 × 0·5) ml of 1 (N) HCl

$\equiv$ 22·2 ml of 1 (N) HCl

Since alkali metals are monovalent, let the molecular formula of the 2 carbonates be M_2CO_3 and N_2CO_3

$\therefore$ Equivalent weight of $M_2CO_3 = \frac{\text{Gram molecular weight}}{2} = \frac{1}{2}$ mole

Equivalent weight of $N_2CO_3 = \frac{\text{Gram molecular weight}}{2} = \frac{1}{2}$ mole

1000 ml of 1 (N) HCl $\equiv$ 1 gram-eq. of carbonate $\equiv \frac{1}{2}$ mole of carbonate

22·2 ml of 1 (N) HCl $\equiv \frac{22\cdot2}{1000 \times 2} = 0\cdot011$ mole of carbonate

Since equal number of moles are present in the mixture

Amount of $M_2CO_3 = \frac{0\cdot0111}{2} = 0\cdot00555$ mole

Amount of $N_2CO_3 = \frac{0\cdot0111}{2} = 0\cdot00555$ mole

Mol. wt. of $M_2CO_3 = 2 \times 7 + 12 + 3 \times 16 = 74$ (Atomic weight of M = 7)

$\therefore$ 0·00555 moles of $M_2CO_3 = 0\cdot00555 \times 74 = 0\cdot4107$ g

$\therefore$ Weight of $N_2CO_3 = 1 - 0\cdot4107 = 0\cdot5893$ g

Again 0·00555 moles of N_2CO_3 = 0·5893 g

$$\text{or, } 1 \text{ mole} = \frac{0{\cdot}5893}{0{\cdot}00555} = 106 \text{ g}$$

Let the atomic weight of N be A

∴ Mol. wt. of $N_2CO_3 = 2A + 60$

or, $2A + 60 = 106$ or, $A = 23$

Hence the atomic weight of N is 23

$$\underset{74\,g}{M_2CO_3} + H_2SO_4 = \underset{110\,g}{M_2SO_4} + CO_2 + H_2O$$

∴ 0·4107 g of M_2CO_3 yields $\frac{110 \times 0{\cdot}4107}{74}$ g of Sulphate

Similarly,

$$\underset{106\,g}{N_2CO_3} + H_2SO_4 = \underset{142\,g}{N_2SO_4} + CO_2 + H_2O$$

or, 0·5893 g of N_2CO_3 yields = $\frac{142 \times 0{\cdot}5893}{106}$ g of Sulphate.

Total weight of the metal sulphates

$$= \frac{110 \times 0{\cdot}4107}{74} + \frac{142 \times 0{\cdot}5893}{106} = 1{\cdot}399 \text{ g}$$

40. *25 ml of a solution of Na_2CO_3 having specific gravity of 1·25 required 32·9 ml of a solution of HCl containing 109·5 g of the acid per litre, for complete neutralisation. Calculate the volume of 0·84 (N) H_2SO_4 that will be completely neutralised by 125 g of the sodium carbonate.* [*J.E.E. 1982*]

Ans : The strength of HCl = $\frac{109{\cdot}5}{36{\cdot}5}$ (N) = 3·0 (N)

Let S_1 be the strength of Na_2CO_3 solution

$25 \times S_1 = 32{\cdot}9 \times 3$ (N)

$S_1 = 3{\cdot}948$ (N)

Volume of 125 g Na_2CO_3 = $\frac{125}{1{\cdot}25}$ = 100 ml.

Let V ml of H_2SO_4 is required to neutralise this 100 ml Na_2CO_3 solution.

$V \times 0{\cdot}84$ (N) = $100 \times 3{\cdot}948$ (N)

$V = 470$ ml of H_2SO_4

41. *134 ml of H_2SO_4 is neutralised by 2 litres of NH_3 at 30°C and 0·9 atmospheric pressure. Calculate the normality of the acid.* [*I.I.T. 1968*]

Ans : Let at N.T.P. the volume of NH_3 be V ml.

$$\frac{V \times 1}{273} = \frac{2 \times 0{\cdot}9}{303}$$

$V = 1{\cdot}622$ litre

22·4 litre of NH_3 at N.T.P. weigh 17 g

1·622 litre of NH_3 at N.T.P. weigh $\frac{17 \times 1{\cdot}622}{22{\cdot}4}$ = 1·231 g

$$\underset{2\times 17\,g}{2NH_3} + \underset{98\,g}{H_2SO_4} = (NH_4)_2SO_4$$

2 × 17 g NH_3 neutralise 98 g of H_2SO_4

1·231 g NH_3 neutralise $\frac{98 \times 1{\cdot}231}{2 \times 17}$ = 3·548 g of H_2SO_4

Again, 134 ml H_2SO_4 contain 3·548 g of H_2SO_4

1000 ml H_2SO_4 contain $\frac{3{\cdot}548 \times 1000}{134}$ = 26·4776 g of H_2SO_4

∴ Strength of H_2SO_4 = $\frac{26{\cdot}4776}{49}$ (N) = 0·5403 (N)

42. *0·11 g of Mg is completely dissolved in 50 ml of seminormal H_2SO_4. The resulting solution is neutralised by 20 ml of 0·8 (N) KOH. What is the equivalent weight of Mg ?* [*Roorkee Ent. Test 1983*]

Ans : 50 ml of $\left(\frac{N}{2}\right)$ $H_2SO_4 \equiv$ 25 ml of (N) H_2SO_4

20 ml of 0·8 (N) KOH $\equiv$ (20 × 0·8) ml of (N) KOH
$\equiv$ 16 ml of (N) KOH

16 ml of (N) KOH neutralise 16 ml of (N) H_2SO_4.

Hence the acid that react with Mg = (25 − 16) = 9 ml of (N) H_2SO_4

or, 9 ml of (N) $H_2SO_4 \equiv$ 0·11 g of Mg

$$1000 \text{ ml of (N) } H_2SO_4 \equiv \frac{0{\cdot}11 \times 1000}{9} = 12{\cdot}2 \text{ g}$$

Hence, the Eq. wt. of Mg = 12·2

43. *1 g of impure Na_2CO_3 is dissolved in water and the solution is made upto 250 ml. To 50 ml of this made up solution 50 ml of 0·1 (N) HCl is added and the mixture after shaking well required 10 ml of 0·16 (N) NaOH solution for complete neutralisation. Calculate the percentage purity of Sodium carbonate in the sample.* [*B.I.T. Mesra 1989*]

Ans : 10 ml of 0·16 (N) NaOH solution $\equiv$ (10 × 0·16) ml of (N) NaOH
$\equiv$ 1·6 ml of (N) NaOH $\equiv$ 16 ml of 0·1 (N) NaOH
$\equiv$ 16 ml of 0·1 (N) HCl

Volume of HCl that reacts with Na_2CO_3 solution
= (50 − 16) = 34 ml of 0·1 (N) HCl

50 ml of Na_2CO_3 solution $\equiv$ 34 ml of 0·1 (N) HCl

$$250 \text{ ml of } Na_2CO_3 \text{ solution} = \frac{34 \times 250}{50} = 170 \text{ ml of 0·1 (N) HCl}$$

= 170 ml of 0·1 (N) Na_2CO_3
= 17 ml of (N) Na_2CO_3

$$17 \text{ ml of 1 (N) } Na_2CO_3 \text{ contains } \frac{53 \times 17}{1000} = 0{\cdot}901 \text{ g of } Na_2CO_3$$

% of pure Na_2CO_3 = 0·901 × 100 = 90·1%

44. *1 g of an impure sample of $CaCO_3$ is treated with 230 ml of $\left(\frac{N}{10}\right)$ HCl. The residual acid for neutralisation requires 8 ml of 0·45 (N) NaOH. Calculate the % of pure $CaCO_3$ in the sample.* [*J.E.E 1988*]

Ans : 230 ml of $\left(\frac{N}{10}\right)$ HCl $\equiv$ 23 ml of (N) HCl

8 ml of 0·45 (N) NaOH $\equiv$ (8 × 0·45) ml of 1 (N) NaOH
$\equiv$ 3·60 ml of (N) NaOH
$\equiv$ 3·60 ml of (N) HCl

Amount of $CaCO_3 \equiv$ (23 − 3·60) = 19·4 ml of (N) HCl

1000 ml of (N) HCl $\equiv$ 50 g of $CaCO_3$ [Eq. wt. of $CaCO_3$ = 50]

$$19{\cdot}4 \text{ ml of (N) HCl} \equiv \frac{50 \times 19{\cdot}4}{1000} = 0{\cdot}97 \text{ g of } CaCO_3$$

% of pure $CaCO_3$ = 97%

45. *25 ml of a mixture of Na_2CO_3 and $NaHCO_3$ is titrated with $\left(\frac{N}{20}\right)$ HCl solution. In presence of phenolphthalein indicator the solution requires 20·5 ml of HCl. To the resulting colourless solution Methyl orange indicator is added. A further quantity of*

29·5 ml of HCl is required to change the colour from yellow to orange. Find the strength of Na_2CO_3 and $NaHCO_3$ in the mixture.

Ans : Total volume of HCl required in the complete neutralisation process

$$= 20{\cdot}5 + 29{\cdot}5 = 50 \text{ ml of } \left(\frac{N}{20}\right) \text{HCl}$$

The end point with phenolphthalein indicator denotes half of the neutralisation point i.e., half of the amount of Na_2CO_3.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$
$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O$$

Total amount of Na_2CO_3 is neutralised by $2 \times 20{\cdot}5 = 41$ ml of $\left(\frac{N}{20}\right)$ HCl

In the mixture $NaHCO_3$ is neutralised by $(50 - 41) = 9$ ml $\left(\frac{N}{20}\right)$ HCl

Let S_1 be the strength of Na_2CO_3 in the mixture

$$25 \times S_1 = 41 \times \frac{N}{20} \quad \text{or,} \quad S_1 = 0{\cdot}082\,(N)$$

Let S_2 be the strength of $NaHCO_3$ in the mixture

$$25 \times S_2 = 9 \times \frac{N}{20} \quad \text{or,} \quad S_2 = 0{\cdot}018\,(N)$$

Hence strength of Na_2CO_3 solution $= 0{\cdot}082$ (N)
and strength of $NaHCO_3$ solution $= 0{\cdot}018$ (N)

46. *When 60 ml of (N) HCl is added to 50 ml of a mixed solution of Na_2CO_3 and NaOH containing a drop of phenolphthalein, the pink colour is just discharged. A few drops of Methyl orange is added to the solution. 20 ml more of same HCl solution when added to it, the solution turns pink. Calculate the strength of Na_2CO_3 and NaOH in gm per litre of the solution.* *[W.B.H.S. 1988]*

Ans : Phenolphthalein indicator shows colour change in the first titration when NaOH is fully neutralised and half of Na_2CO_3 is neutralised. Na_2CO_3 converted into $NaHCO_3$.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

In the second titration when $NaHCO_3$ is neutralised, Methyl orange shows change of colour from yellow to pink.

$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O$$

(The amount of $NaHCO_3$ is half the amount of Na_2CO_3)
Volume of HCl required in the first titration = 60 ml of (N) HCl
This volume of HCl neutralise full NaOH and ½ the amount of Na_2CO_3.
In the second titration 20 ml of (N) HCl neutralise ½ the amount of Na_2CO_3.

$\therefore$ Amount of NaOH is 50 ml mixture $\equiv (60 - 20) \equiv 40$ ml of (N) HCl
$\equiv 40$ ml of (N) NaOH

$$\therefore \text{ Weight of NaOH in 40 ml} = \frac{40 \times 40}{1000} = 1{\cdot}6 \text{ g}$$

Again amount of Na_2CO_3 in 50 ml mixture
= Double the volume of acid in the second titration
$\equiv (2 \times 20) \equiv 40$ ml of (N) HCl
$\equiv 40$ ml of (N) Na_2CO_3

$$\text{Weight of } Na_2CO_3 \text{ in 40 ml} = \frac{40 \times 53}{1000} = 2{\cdot}12 \text{ g}$$

Now 50 ml mixture contain 1·6 g of NaOH

$$1000 \text{ ml mixture contain } \frac{1{\cdot}6 \times 1000}{50} = 32{\cdot}0 \text{ g of NaOH}$$

Again 50 ml of the mixture contain 2·12 g of Na_2CO_3

$$1000 \text{ ml of the mixture contain } \frac{2{\cdot}12 \times 1000}{50} = 42{\cdot}4 \text{ g of } Na_2CO_3$$

47. *The molarity of a solution of Na_2CO_3 is 0·408 M at 20°C. Calculate the molality of the solution (Density of the solution at 20°C is 1·0816 g/ml).* [*W.B.J.E.E. 1987*]

Ans : 1000 ml of Na_2CO_3 contain $106 \times 0{\cdot}408 = 43{\cdot}248$ g of Na_2CO_3
Weight of 1000 ml solution $= 1000 \times 1{\cdot}0816 = 1081{\cdot}6$ g
Weight of solvent (water) $= 1081{\cdot}6 - 43{\cdot}248 = 1038{\cdot}352$ g

Number of moles of $Na_2CO_3 = \dfrac{43{\cdot}248}{106}$

1038·352 g of water contain $\dfrac{43{\cdot}248}{106}$ moles of Na_2CO_3

1000 g of water contain $\dfrac{43{\cdot}248 \times 1000}{106 \times 1038{\cdot}352} = 0{\cdot}393$ molal.

48. *8·25 g of a saturated solution of Na_2CO_3 at 27°C required 138 ml of 0·25 (N) HCl for complete neutralisation. Calculate the solubility of Na_2CO_3 at 27°C.* [*W.B.J.E. '96*]

Ans. 138 ml of 0·25 (N) HCl $\equiv 138 \times 0{\cdot}25$ ml of (N) HCl
$\equiv 34{\cdot}5$ ml of (N) HCl
$\equiv 34{\cdot}5$ ml of (N) Na_2CO_3
1000 ml of (N) Na_2CO_3 solution contains 53 g of Na_2CO_3

34·5 ml of (N) Na_2CO_3 solution contains $\dfrac{53 \times 34{\cdot}5}{1000}$ g of $Na_2CO_3 = 1{\cdot}8285$ g of Na_2CO_3

$\therefore$ Amount of water in 8·25 g of Na_2CO_3 solution $= (8{\cdot}25 - 1{\cdot}8285) = 6{\cdot}4215$ g
At 27°C, 6·4215 g of water is saturated by 1·8285 g of Na_2CO_3

At 27°C, 100 g of water is saturated by $\dfrac{1{\cdot}8285 \times 100}{6{\cdot}4215} = 28{\cdot}47$ g of Na_2CO_3

$\therefore$ Solubility of Na_2CO_3 at 27°C is 28·47.

49. *10 ml of a solution of HCl exactly neutralise 40·0 ml of a (N) NaOH solution. In another 20 ml of the same HCl solution,, 2·00 g of lime stone is completely dissolved. The resulting acidic solution requires 41·0 ml of (N) NaOH for exact neutralisation. Calculate the percentage by weight of $CaCO_3$ in the sample of lime stone. Assume that only the $CaCO_3$ in lime stone and not the impurities in lime stone reacts with the given HCl solution.* [*J.E.E. 1990*]

Ans : $10 \times S = 40 \times N$

$S = \dfrac{40}{10}$ N,

or, the strength of HCl $= \dfrac{40}{10}$ (N) $= 4{\cdot}0$ (N)

20 ml of 4 (N) HCl $\equiv$ 80 ml of (N) HCl
2·00 g of lime stone is dissolved in 80 ml of (N) HCl
Excess acid that does not react with $CaCO_3 \equiv$ 41 ml of (N) NaOH
$\equiv$ 41 ml of (N) HCl

$\therefore$ Volume of acid that react with $CaCO_3 = (80 - 41) = 39$ ml of (N) HCl

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

Eq. wt. of $CaCO_3 = 100/2 = 50$
1000 ml of (N) HCl $\equiv$ 50 g of $CaCO_3$

39 ml of (N) HCl $\equiv \dfrac{50 \times 39}{1000} = 1{\cdot}95$ g of $CaCO_3$

% of pure $CaCO_3 = \dfrac{1{\cdot}95 \times 100}{2{\cdot}0} = 97{\cdot}5\%$

50. *1·575 g of $(COOH)_2\,xH_2O$ are dissolved in water and the volume made upto 250 ml. On titration with 16·68 ml of this solution 25 ml of $\left(\frac{N}{15}\right)$ NaOH solution are required for exact neutralisation. Calculate the value of x (i.e. Number of water molecules).* *[B.I.T. Mesra 1987]*

Ans : 250 ml of the solution contain 1·575 g

1000 ml of the solution contain $\frac{1·575 \times 1000}{250} = 6·3$ g

Applying the formula, $V_1S_1 = V_2S_2$

$$25 \times \frac{N}{15} = 16·68 \times S_2$$

Or, the strength of the acid = $\frac{25}{16·68 \times 15}$(N) = $\frac{1}{10·008}$ (N)

We know, Gram/litre = Normality × Eq. wt.

or, Eq. wt. of the acid = $\frac{\text{Gram/litre}}{\text{Normality}} = 6·3 \times 10·008 = 63$ (Approx.)

Since the acid contain two replaceable hydrogen atoms, its basicity = 2

∴ Mol. wt. of the acid = 63 × 2 = 126

$(COOH)_2xH_2O = 126$

$90 + 18x = 126$

∴ $x = 2$

Hence the value of $x = 2$.

or, the molecular formula of the acid is $(COOH)_2.2H_2O$

51. *1·0 g sample of Fe_2O_3 of 55·2 percent purity is dissolved in acid and reduced by heating the solution with Zn dust. The resultant solution is cooled and made up to 100 ml. An aliquot of 25 ml of this solution requires 17 ml of 0·0167 (M) solution of an oxidant for titration. Calculate number of electrons taken up by the oxidant in the reaction of the above titration.* *[I.I.T. '91]*

Ans : Weight of pure Fe_2O_3 in the sample = $\frac{55·2 \times 1}{100} = 0·552$ g

Number of moles of $Fe_2O_3 = \frac{0·552}{159·8} = 3·454 \times 10^{-3}$

Number of moles of Fe^{3+} ions = $2 \times 3·454 \times 10^{-3} = 6·908 \times 10^{-3}$ mole.

Now, as the conversion of Fe^{3+} to Fe^{2+} involves only one electron transfer

$Fe^{3+} + e \rightarrow Fe^{2+}$, the molecular wt. will be the same as its equivalent wt.

∴ Amount of Fe^{2+} ion in 100 ml = $6·908 \times 10^{-3}$ equivalents = 6·908 milli eq.

Volume of oxidant used for 100 ml of Fe^{2+} solution = 17 × 4 = 68 ml

∴ Amount of oxidant used = 68 × 0·0167 milli mole.

Let the number of electron taken by the oxidant = x

∴ No. of milli eq. of oxidant used = $68 \times 0·0167x = 1·1356x$

Thus $1·1356x = 6·908$

or, $x = 6$

52. *0·5 g of oleum is diluted with water. This solution is completely nutralised by 26·7 ml of 0·4 N NaOH. Find the percentage of free SO_3 in the sample solution.* *[I.I.T., '80]*

Ans : Oleum $H_2S_2O_7 = SO_3 + H_2SO_4$

Reaction between SO_3 (H_2SO_4) and NaOH is given by—

$$2NaOH + SO_3 = Na_2SO_4 + H_2O$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

Let the weight of free SO_3 in oleum = x g

∴ The wt. of H_2SO_4 in 0·5 g oleum = $(0·5 - x)$ g

$$\text{Eq. wt. of } SO_3 = \frac{\text{mol. wt.}}{2} = \frac{80}{2} = 40. \quad (\because\ SO_3 + H_2O = SO_4^{2-} + 2H^+)$$

Now 1 gram eq. of $SO_3 \equiv$ 1 gram eq. of NaOH $\equiv$ 1000 ml of (N) NaOH
i.e., 40 g of $SO_3 \equiv$ 1000 ml of (N) NaOH

$$\therefore\ x \text{ g of } SO_3 \equiv \frac{1000x}{40} \text{ ml} = 25x \text{ ml of (N) NaOH}$$

Again, 1 gram eq. of $H_2SO_4 \equiv$ 1000 ml of (N) NaOH
or, 49 g of $H_2SO_4 \equiv$ 1000 ml of (N) NaOH

$$\therefore\ (0{\cdot}5 - x) \text{ g of } H_2SO_4 \equiv \frac{1000\,(0{\cdot}5 - x)}{49} \text{ ml of (N) NaOH}$$

$$\text{Total volume} = 25x + \frac{1000\,(0{\cdot}5 - x)}{49}$$

Now 26·7 ml of 0·4 (N) NaOH $\equiv 26{\cdot}7 \times 0{\cdot}4$ ml of (N) NaOH
$\equiv$ 10·68 ml of (N) NaOH

$$\therefore\ 25x + \frac{1000\,(0{\cdot}5 - x)}{49} = 10{\cdot}68$$

or, $25x + 20{\cdot}408\,(0{\cdot}5 - x) = 10{\cdot}68$
or, $25x + 10{\cdot}204 - 20{\cdot}408x = 10{\cdot}68$
or, $4{\cdot}592x = 0{\cdot}476$
or, $x = 0{\cdot}1036$

$$\text{Hence \% of free } SO_3 = \frac{0{\cdot}1036 \times 100}{0{\cdot}5} = 20{\cdot}72$$

53. *4·08 g of a mixture of BaO and an unknown carbonate MCO_3 was heated strongly. The residue weighed 3·64 g. This was dissolved in 100 ml of 1 (N) HCl. The excess acid required 16 ml of 2·5 NaOH soln. for complete neutralisation. Identify the metal M. [Ba=138]* *[I.I.T. '83]*

Ans :

$$\underset{\text{1 mole}}{MCO_3} \xrightarrow{\text{heat}} \underset{\text{1 mole}}{MO} + \underset{\text{1 mole}}{CO_2}$$

Thus we see that 1 mole of carbonate thermally decomposed to give 1 mole of MO and 1 mole of CO_2. So the carbonate will loose weight due to the evolution of CO_2. BaO will remain unchanged.

From data, loss of wt. = 4·08 − 3·64 = 0·44 g.
0·44 g of CO_2 = 0·44/44 = 0·01 mole.
From equation we see—
1 mole of $CO_2 \equiv$ 1 mole of MCO_3
$\therefore$ 0·01 mole of $CO_2 \equiv$ 0·01 mole of MCO_3

Thus the given mixture contains 0·01 mole of MCO_3 which gives 0·01 mole of MO
$\equiv$ Now, 16 ml of 2·5 (N) NaOH = 16 × 2·5 ml of (N) NaOH
$\equiv$ 40 ml of (N) NaOH $\equiv$ 40 ml of (N) HCl
The vol of HCl remain unused = 40 ml
$\therefore$ The vol of HCl used = 100 − 40 = 60 ml of (N) HCl
This 60 ml of (N) HCl is used in neutralising BaO and MO.

$$\underset{\text{1 mole}}{MO} + \underset{\text{2 mole}}{2HCl} = MCl_2 + H_2O$$

Thus 0·01 mole of MO $\equiv$ 0·02 mole of HCl
When 1 mole of HCl is present in 1000 ml the strength of HCl is N.
$\therefore$ When 0·02 mole of HCl is present in 1000 × 0·02 ml = 20 ml the strength of (N) HCl.
Vol of HCl used to react with MO is 20 ml
$\therefore$ Vol of HCl used to react with BaO = (60 − 20) = 40 ml.

$$\text{Eq. wt. of BaO} = \frac{138 + 16}{2} = 77$$

40 ml of (N) HCl $\equiv$ 40 ml of (N) BaO

1000 ml of (N) BaO contains 77 g of BaO

$$40 \text{ ml of (N) BaO contains } \frac{77 \times 40}{1000} = 3{\cdot}08 \text{ g of BaO}$$

Total wt. of oxides = 3·64 g

$\therefore$ Wt. of MO = 3·64 − 3·08 = 0·56 g

Now, 0·01 mole of MO is present in the residue

i.e., 0·01 mole of MO = 0·56 g

$$1 \text{ mole of MO} = \frac{0{\cdot}56}{0{\cdot}01} = 56 \text{ g of MO}$$

Let the atomic wt. of M = a

$\therefore$ the molecular wt. of MO = $a + 16$.

or, $a + 16 = 56$ or, $a = 40$

The atomic weight of the metal M = 40.

$\therefore$ The metal is calcium.

54. *A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 ml of water. 10 ml of this soln. was reacted with excess of $FeCl_3$ soln. and warmed to complete the reaction. Ferrous ions formed was estimated and it required 20 ml of M/50 $KMnO_4$ soln. Estimate the amount of hydrazine sulphate in 1 litre of soln.*

Reaction :

$$4Fe^{3+} + N_2H_4^- \rightarrow N_2 + 4Fe^{2+} + 4H^+$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

[*I.I.T. '88*]

Ans : $\overset{+2}{N_2H_4} \rightarrow \overset{0}{N_2}$

$$\text{Eq. wt. of } N_2H_6SO_4 = \frac{130}{4} = 32{\cdot}5$$

$$\text{Eq. wt. of } KMnO_4 = \frac{158}{5} = 31{\cdot}6$$

$$20 \text{ ml M/50 } KMnO_4 \text{ contain } \frac{158 \times 20}{50 \times 1000} \text{ g of } KMnO_4 = 0{\cdot}0632 \text{ g.}$$

$$\text{No. of equivalent} = \frac{0{\cdot}0632}{31{\cdot}6} = 0{\cdot}002$$

Let the amount of hydrazine sulphate be x g

$$\therefore \text{ No. of equivalent of hydrazine sulphate} = \frac{x}{32{\cdot}5}$$

$$\therefore \frac{x}{32{\cdot}5} = 0{\cdot}002 \quad \text{or, } x = 0{\cdot}065 \text{ g}$$

Hence the wt. of $N_2H_6SO_4$ in 10 ml = 0·065 g

Weight of hydrazine sulphate in 1000 ml = 6·5 g

55. *An equal volume of a reducing agent is titrated separately with 1(M) $KMnO_4$ in acid, neutral and alkaline media. The volumes of $KMnO_4$ required are 20 ml in acid, 33·4 ml is neutral and 100 ml in alkaline media. Find out the oxidation state of Mn in each reduction product. Give balanced equations for all three half reactions. Find out the volume of 1 (M) $K_2Cr_2O_7$ consumed if the same volume of reducing agent is titrated in acid media.* [*I.I.T. '89*]

Ans : Let the normality of $KMnO_4$ in acid, neutral and alkaline media be N_1, N_2 and N_3 respectively.

$\therefore 20\,N_1 \equiv 33{\cdot}4\,N_2 \equiv 100\,N_3$............................(1)

Reaction of reduction of $KMnO_4$ in acid media is

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

$\therefore$ 1(M) $KMnO_4 \equiv$ 5(N) $KMnO_4$

From (1) we get $20\,N_1 \equiv 33{\cdot}4\,N_2$

$$\text{or, } N_2=\frac{20\,N_1}{33\cdot4}=\frac{20\times5N}{33\cdot4}=2\cdot99\,N$$

$$\text{Again, } 20\,N_1\equiv100\,N_3 \qquad \text{or, } N_3=\frac{20\,N_1}{100}$$

$$\text{or, } N_3=\frac{20\times5N}{100}=1N$$

The equation in the there media may be written as

$$MnO_4^- + 5e \xrightarrow{acid} Mn^{2+}$$

$$MnO_4^- + 3e \xrightarrow{\text{neutral}} Mn^{4+}$$

$$MnO_4^- + e \xrightarrow{\text{alkaline}} Mn^{6+}$$

The oxidation state of the reduction products in acidic, neutral and alkaline media are +2, +4 and +6 respectively.

The balanced equations for the 3 half reactions are—

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$$

$$MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4OH^-$$

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}$$

Reaction of $K_2Cr_2O_7$ in acid media

$$Cr_2O_7^{2-} + 14H + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$1\,(M)\,Cr_2O_7^{2-} \equiv 6\,(N)\,Cr_2O_7^{2-}$$

$$\therefore \text{Vol. of } 1\,(M)\,K_2Cr_2O_7=\frac{20\times N_1}{6N}=\frac{20\times5N}{6N}=16\cdot66\text{ ml}$$

56. *A mixture of oxalic acid and $NaHC_2O_4$ weighing 2·02 g was dissolved in water and the soln. made upto 1 litre. 10 ml of the soln. required 3 ml of 0·1 (N) NaOH soln. for complete neutralisation. In another experiment, 10 ml of the same soln. in hot dilute H_2SO_4 medium, required 4 ml of 0·1 (N) $KMnO_4$ soln. for complete reaction. Calculate the amount of oxalic acid and NaH_2CO_4 in the mixture.* [*I.I.T. '90*]

Ans : Reactions :— (i) $H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$

(ii) $NaHC_2O_4 + NaOH \rightarrow Na_2C_2O_4 + H_2O$

Let the normality of the mixture is N,

$\therefore$ $10\times N_1=3\times0\cdot1$ or, $N_1=0\cdot03$

In second case, the reaction is—

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$KMnO_4$ will react in the same manner both with $NaHC_2O_4$ and $H_2C_2O_4$ as shown in the above reactions.

Let the normality of the mixture when titrated with $KMnO_4$ be N_2. Therefore in this case

$$4\times0\cdot1N=10\times N_2 \qquad \text{or, } N_2=0\cdot04.$$

The difference in normality = 0·04 − 0·03 = 0·01.

This is due to $NaHC_2O_4$

$\therefore$ The total normality of $NaHC_2O_4 = 0\cdot01 + 0\cdot01 = 0\cdot02N$

$$\text{Eq. wt. of } NaHC_2O_4=\frac{112}{2}=56$$

$\therefore$ The amount of $NaHC_2O_4$ in 1 litre = 0·02 × 56 = 1·12 g

Amount of $H_2C_2O_4$ = 2·02 − 1·12 = 0·9 g

• Exercises •

1. Explain with examples the following terms—(i) equivalent weight of acid, (ii) equivalent wt. of base and (iii) equivalent wt. of salt. Determine the equivalent weight of Acetic acid, Calcium hydroxide and Aluminium sulphate.

2. Define (i) Normal solution, (ii) Molar solution and (iii) Molal solution Distinguish between molar solution and molal solution. In which case a normal solution becomes a molar solution ?

3. (i) Define (a) Normality, (b) Molarity, (c) Molality, (d) Molar fraction, (e) Formality.

(ii) Distinguish between a Molar solution and Formal solution. [*W.B.H.S. '91*]

4. What is standard solution ? What should be the essential qualities of a primary standard substance ? How would you prepare 200 ml of exactly 0·1(N) Na_2CO_3 solution ?

5. What is an acid base indicator ? Which indicator would you use in the following titrations and why ?
(a) An aqueous solution of HCl with Na_2CO_3 solution. [*Joint Ent. '89*]
(b) An aqueous solution of acetic acid with caustic soda solution. [*Joint Ent. '82*]
(c) An aqueous solution of oxalic acid with NaOH solution. [*Joint Ent. '89*]

6. (a) What is neutralisation reaction ? Show that a neutral solution contains neither H^+ nor OH^- ions.

7. Explain why : [*Joint Ent. '84*]
(i) 10 g of pure NaOH neutralise a larger quantity of HCl than 10 g of pure Na_2CO_3.
(ii) Standard solution of NaOH and HCl can not be prepared by direct weighing.
(iii) H_2SO_4 is a secondary standard while oxalic acid is a primary standard solution.
(iv) 25 ml of 10% HCl does not neutralise 25 ml 10% NaOH solution.
(v) The basicity of an acid does not indicate the number of hydrogen atom contained in it.
(vi) Equal volume of acids and bases having equal normality neutralise each other.
(vii) 1(N) HCl is a standard solution.
(viii) The strength of NaCl is expressed in terms of formality but not in molarity.
(ix) No indicator is suitable in titration of weak acid against a weak base.

8. (i) You find bottles marked 'conc. H_2SO_4', conc. HCl as also 'dil. H_2SO_4', 'dil. HCl' in the reagent racks of your laboratory. What are the approximate strength in normalities of these acids ?
(ii) How can you prepare 360 ml of that 'dil. H_2SO_4' from the 'conc H_2SO_4'. [*Joint Ent. '91*]

9. Which of the following solutions has the greater normality.
(i) A soln. of HCl containing 0·0356 g ml^{-1}.
(ii) A soln. of H_2SO_4 containing 0·098 g ml^{-1}. [***Ans.*** H_2SO_4, 2N] [*Joint Ent. '89*]
(iii) What is the mole fraction of a solute in 1 molal soln. of water ? [***Ans.*** 0·0176]

10. 10 cc of N/10 Na_2CO_3 solution is titrated with N/10 HCl solution from a burette using.
(i) Methyl orange indicator. (ii) Phenolphthelein indicator.
Will the two burette reading be the same ? If not why not ? Explain your answer. [*W.B.J.E. '97*]

- **Numerical problems :**

1. Express the strength of the following solution in terms of normality and molarity—
(i) 5% NaOH, (ii) 0·049 g of H_2SO_4 in 500 ml, (iii) 10 g NaOH per litre.
[***Ans.*** (i) 1·25(N), 1·25(M), (ii) 0·002(N), 0·001(M), (iii) 0·25(N), 0·25(M)]

2. Calculate the weight of the solute in grams in the following solutions—
(i) 250 ml of 5% NaOH, (ii) 400 ml of 2F NaCl, (iii) 50 ml of 0·75(M) KOH.
[***Ans.*** (i) 12·5 g, (ii) 46·8 g, (iii) 2·1 g]

3. Find the equivalent weight of the solute in the following solutions—
(i) 1·575 g of N/10 oxalic acid in 250 ml, (ii) 3·65 g of 10(N) HCl in 10 ml, (iii) 11·2 g of 0·2(N) KOH in 1 litre. [***Ans.*** (i) 63, (ii) 36·5, (iii) 56]

4. Find the weight of Na_2CO_3 in gram. required to prepare the following solutions—
(i) 250 ml of (N/10) Na_2CO_3, (ii) 500 ml of 0·5(M) Na_2CO_3 [*H.S. '80*], (iii) 1000 ml of 5% Na_2CO_3 [*I.S.C. '84*], (iv) 100 ml of 1(F) Na_2CO_3. [***Ans.*** (i) 1·325 g, (ii) 26·5 g, (iii) 10·6 g, (iv) 99·37 g]

5. 25 ml of 0·1(M) NaOH soln. neutralises 22·5 ml of solution of HCl. How much water is to the added to 500 ml of the HCl solution to make it exactly 0·1N ? [***Ans.*** 55·5 ml] [*H.S. '80*]

6. A bottle of commercial sulphuric acid is lebelled '86% H_2SO_4'. Its density is 1·787 g/ml. What is the molarity of the acid solution ? What volume of this acid is needed to make 1 litre of 0·2(M) H_2SO_4 ?
[***Ans.*** 15·68(M), 12·75 ml] [*I.I.T. '79, H.S. '79*]

7. A bottle in the laboratory is marked 12(N) HCl. How could you prepare 20 ml of 3 (N) HCl from this HCl ? [***Ans.*** 5 ml of this acid to be diluted to 20 ml] [*H.S. '78*]

8. Find the volume of 10% NaOH soln. which would neutralise 500 ml of HNO_3 containing 6·3 g of HNO_3 per litre. [***Ans.*** 20 ml]

9. The specific gravity of a sample of HCl is 1·16. It contains 32% of HCl. Find the volume of this acid required to prepare 1 litre of (N) HCl. [***Ans.*** 98·33 ml]

10. 25 ml of 0·08(N) NaOH is mixed with 20 ml of 0·09(N) Na_2CO_3. Find the normality of the resulting solution. 30 ml of this mixed alkali neutralise 50 ml of a H_2SO_4 soln. Find the normality of the acid.
[***Ans.*** 0·084(N), 0·0504(N)]

11. The specific gravity of 61% by weight of nitric acid is 1·41. Determine its normality.
[***Ans.*** 13·65N] [*H.S. '91*]

12. A solution is prepared by dissolving 0·53 g of Na_2CO_3 in 250 ml of water. 1500 ml of (N/10) H_2SO_4 is mixed to this solution. Find the normality of the resulting solution. [***Ans.*** 0·08(N)]

13. 0·53 g of Na_2CO_3 is added to 100 ml of (N/10) H_2SO_4 (f=1·25). State whether the resulting solution is acidic or alkaline. Calculate the volume 0·75 (N/10) acid or alkali required to neutralise the solution.
[***Ans.*** acidic, 33·3 ml]

14. 25 ml of 0·18(N) NaOH is mixed with 30 ml of a solution of H_2SO_4. 10 ml of 0·096(N) Na_2CO_3 is further added to neutralise the solution completely. Calculate the strength of H_2SO_4 in gram litre^{-1}. Find also the weight of Na_2SO_4 formed in the solution. [*Ans.* 8·918 g lit^{-1}, 0·387 g]

15. 10 ml of a conc. H_2SO_4 is dissolved in water and the volume made up to 1 litre. 28·8 ml 0·25(N) Na_2CO_3 is required to neutralise 20 ml of the above diluted acid. Calculate the volume of the diluted acid to be diluted to 1 litre to make the resulting solution exactly 0·1(N). [*Ans.* 277·78 ml]

16. 1·4175 g of a dibasic acid is dissolved in water and the volume made up to 250 ml. 16·9 ml of 0·12(N) NaOH is required to neutralise 22·5 ml of the acid. Find the equivalent weight and atomic weight of acid. [*Ans.* 63, 126]

17. A specimen of impure sodium carbonate contains 90% Na_2CO_3 and 10% $NaHCO_3$. Find the weight of this specimen dissolved in water to make the volume 1 litre which is neutralised by (N/5) H_2SO_4 of the same volume. [*Ans.* 11·011 g]

18. Some $CaCO_3$ was dissolved in 525 ml of N/10 HCl so that no excess acid was left after the reaction. $CaCl_2$ thus formed during the reaction was converted into $CaSO_4$. Find the weight of $CaCl_2$ and plaster of paris. [*Ans.* 2·914 g and 3·806 g]

19. 0·21 g of a metal is dissolved in 100 ml of 0·5(N) H_2SO_4. 32·5 ml of (N) alkali were required to neutralise the excess acid. Find the equivalent weight of the metal. [*Ans.* 12]

20. 0·475 g of a mixture of Na_2CO_3 and $NaHCO_3$ solution is titrated with 0·5(N) H_2SO_4 in presence of methyl orange indicator. Exactly 15 ml of acid were required for neutralisation. Find the percentage of Na_2CO_3 in the mixture. [*Ans.* 55·8%]

21. A solution contains Na_2CO_3 and $NaHCO_3$. 10 ml of the solution required 2·5 ml of 0·1(M) H_2SO_4 for neutralisation using phenolpthalein indicator. Methyl orange is then added when further 2·5 ml of 0·2(N) H_2SO_4 was required. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in 1 litre of the solution. [*Ans.* Na_2CO_3 = 5·3 g, $NaHCO_3$ = 4·2 g] [*I.I.T. '79*]

22. 0·5 g of a mixture of K_2CO_3 and $LiCO_3$ required 30 ml of 0·25(N) HCl solution for neutralisation. What is the percentage composition of the mixture ? [*Ans.* K_2CO_3 = 96%, $LiCO_3$ = 4%] [*Roorkee Eng. '84*]

23. 1·08 g of NH_4Cl is boiled with 62 ml of (N/2) NaOH to expel NH_3 completely. 44 ml of (N/4) HCl solution is required to neutralise the excess alkali. Calculate the percentage of ammonia in NH_4Cl. [*Ans.* 31·5%]

24. 25 ml of a solution of $(NH_4)_2SO_4$ is boiled with excess of NaOH soln. The NH_3 liberated is passed through 50 ml of 0·5(N) HCl. 13·2 ml of 0·5(N) NaOH are required to neutralise the excess acid. Calculate the weight of $(NH_4)_2SO_4$ in the solution. [*Ans.* 48·576 g]

25. What volume at N.T.P. of gaseous NH_3 will be required to pass into 30 ml of (N)H_2SO_4 solution to bring down the acid strength of this solution to 0·2N ? [*Ans.* 537·6 ml] [*M.L.N.R. '91*]

26. 40 ml of (N/4) HNO_3 were required to neutralise 1·578 g of hydrated barium hydroxide dissolved in water. Find water of crystallisation of barium hydroxide. (Ba = 137·4) [*Ans.* 8]

27. Equal weights of NaOH and KOH are dissolved separately in equal volume on water. Calculate the ratio of their molarities. [*Ans.* 7 : 5]

28 7·1 g of a dibasic acid is dissolved in 1 litre solution. 40 ml of such solution is neutralised by 44·36 ml of 0·1075(N) NaOH. Find out the molecular wt. of the acid. [*Ans.* 119·12]

29. 30 ml of (N/10) HCl is required to neutralise 25 ml of a solution containing NaOH and Na_2CO_3 in presence of phenolpthalein indicator. A further quantity of 10 ml acid is required to neutralise when mythyl orange is used. Calculate the percentage of NaOH in the mixture.

30. A piece of Aluminium weighing 2·7 g is heated with 75 ml of H_2SO_4 (specific gravity 1·18 containing 24·7% H_2SO_4 by weight). After dissolving the metal the volume of the solution is made up to 400 ml by adding water. Determine the molarity of H_2SO_4 present in the prepared solution. (Al—27, S—32) [*Ans.* 0·183(M)] [*Joint Ent. '91*]

31. 10 ml of a solution of HCl exactly neutralises 40 ml of (N) NaOH soln. In another 20 ml of the same HCl soln. 2 g limestone is completely dissolved. The resulting acidic solution requires 41 ml of (N) NaOH for exact neutralisation. Calculate the percentage by wt. of $CaCO_3$ in the sample of limestone. Assume that only the calcium carbonate in limestone and not the impurities in limestone, react with the given acid solution. [*Ans.* 97·5%] [*Joint Ent. '90*]

32. 0·02 gram atom of zinc is dissolved in 181 ml of dilute H_2SO_4. It requires 35 ml of 0·15(N) NaOH for complete neutralisation. Calculate the normality of the acid and weight of $ZnSO_4$. [*Ans.* 0·249(N), 3·22 g of $ZnSO_4$]

33. 5 g of impure calcium carbonate is dissolved in 100 ml of 1(N) HCl. After the reaction is over, the excess acid is neutralised with 25 ml of 0·1(N) NaOH. Find the percentage of impurity in $CaCO_3$. [*Ans.* 2·5%] [*Joint Ent. '84*]

34. 11·2 g of a mixture of Na_2CO_3 and $NaHCO_3$ is dissolved in water and the volume is made up to 1·5 litre. 25 ml of this alkali soln. requires 24·8 ml of 0·101(N) HCl in presence of methyl orange indicator. Find the weight of Na_2CO_3 and $NaHCO_3$ in the mixture. [*Ans.* 2·4347 g, 8·7653 g] [*Puna Board '80*]

35. When 0·3363 g of a metal reacts with 73 ml of water, 190 ml of H_2 gas is evolved at 300K and 720 mm pressure. Find the eq. wt. of the metal and the molarity of the resulting solution.
[***Ans.*** Eq. wt. 23·03, 0·2(M)] [*Cal. Univ.* '52]

36. 69·0 ml of 0·25(N) H_2SO_4 neutralise a standard solution obtained by dissolving 4·125 g of metallic carbonate at 27°C. The equivalent wt. of the metallic carbonate is 53. Calculate the solubility of the metallic carbonate. [***Ans.*** solutility 28·57] [*Bombay F-Y* '53]

37. 1·216 g of $(NH_4)_2SO_4$ are dissolved by excess of NaOH solution and heated. The whole of NH_3 evolved is passed into 100 ml of (N) H_2SO_4 which require 81·6 ml of (N) NaOH for complete neutralisation. Calculate the percentage of NH_3 in $(NH_4)_2SO_4$. [***Ans.*** 25·72%] [*Joint Ent.* '87]

38. In just sufficient quantity of water 2 g of NaOH and 2 g of crystalline oxalic acid are dissolved. What will be the nature of the mixed solution—acidic or alkaline ? [***Ans.*** Alkaline] [*Joint Ent.* '87]

39. In what proportion, 0·5(N) soln. of an acid is to be mixed with 0·3(N) alkali so that the resulting solution will be 0·05(N) alkaline ? [***Ans.*** 5 : 11] [*H.S.* '85]

40. A sample of Mg containing some MgO as impurity was dissolved in 125 ml of (N/10) H_2SO_4. The volume of H_2 evolved at 300·3K and 1 atmosphere pressure was 120·1 ml. The resulting soln. was found to be 0·02(N) with respect to H_2SO_4. Calculate (i) the wt. of the sample dissolved and (ii) the percentage by wt. of Mg in the sample (neglect any change in volume). [***Ans.*** (i) 0·1185 g, (ii) 95·94%] [*I.I.T.* '77]

41. 0·12 g of a metal was dissolved in 25 ml of (N/2) HCl. The resulting solution required 25 ml of (N/10) NaOH for complete neutralisation. What is the equivalent wt. of the metal ? [***Ans.*** 12] [*Joint Ent.* '89]

42. Exactly 400 ml of a HCl soln. when acted upon by an excess of zinc, evolved 2430 ml of H_2 gas, measured over water at 21°C and 747·5 mm pressure. What is the molarity of the acid ? Vapour pressure of water at 21°C=18·6 mm. [***Ans.*** 0·483 M]

43. Given $2S_2O_3^{--}+I_2 \rightleftharpoons 2I^{-}+S_4O_6^{--}$. How many grams of iodine are present in a solution which requires 40 ml of 0·112(M) $Na_2S_2O_3$ to react with it ? [***Ans.*** 0·57 g]

44. 0·518 g of a sample of limestone is dissolved and then the calcium is precipitated as calcium oxalate (CaC_2O_4). After filtering and washing the precipitate, it requires 40 ml of 0·5(M) $KMnO_4$ solution acidified with dil. H_2SO_4 to titrate it. What is the percent of CaO in the limestone ? [***Ans.*** 54·2%]

45. How many ml of 0·1(N) HCl are required to neutralise the NH_3 evolved from 0·5 g of a substance containing 4% nitrogen so that 5 ml of 0·11(N) NaOH solution is consumed for back titration of the excess HCl ?
[***Ans.*** 20 ml]

46. A certain amount of gaseous ammonia is passed into 20 ml of 0·00786(N) HCl. The excess acid is back titrated with 6·3 ml of NaOH, one ml of which is equivalent to 1·025 ml of the HCl soln. Determine the amount of NH_3 that is absorbed by the HCl solution. [***Ans.*** 0·0866 g]

47. Water is added to 25 ml of 6% Na_2CO_3 solution and the volume made up to 250 ml. By using methyl orange indicator it is found that 25 ml of this dilute solution neutralises 30·1 ml of H_2SO_4 solution. (a) Find the pH and normality of H_2SO_4 solution. (b) How much Na_2SO_4, $10H_2O$ will be obtained in the neutral solution ? (c) What volume of H_2SO_4 will show the end point when phenolpthalien indicator is used ? At his stage which salts and in what quantities will be found to be present in the solution ?
[***Ans.*** (a) pH=1·03, 0·094(N), (b) 0·4556 g, (c) 15·05 ml. 0·1188 g] [*Joint Ent.* '92]

48. The weight of a mixture of Na_2CO_3 and $NaHCO_3$ is 22 g. When excess of HCl solution is added to the mixture, 6 litre of CO_2 is evolved at 25°C and 0·947 atmosphere pressure. Find the percentage of Na_2CO_3 in the mixture. [***Ans.*** 54·327%] [*Joint Ent.* '93]

49. 25 g of a sample of $FeSO_4$ was dissolved in water containing dil. H_2SO_4 and the volume made up to 1 litre. 25 cc of this solution required 20 cc of (N/10) $KMnO_4$ soln. for complete oxidation. Calculate the percentage of $FeSO_4$, $7H_2O$ in the sample (Fe 56, Mn 55) [***Ans.*** 88·96%] [*Roorke Eng.* '82]

50. 5·39 g of a mixture of $FeSO_4$, $7H_2O$ and anhydrous ferric sulphate required 80 ml of 1·25N permanganate soln. for complete conversion to feric sulphate. Calculate the individual weights of each component of the original mixture. [***Ans.*** $FeSO_4$ $7H_2O$=2·78 g, $Fe_2(SO_4)_3$=2·61 g] [*I.I.T.* '73]

51. In what proportion by volume 0·2 N NaOH solution is to be mixed with 0·3 N NaOH solution so that the resulting solution will be 0·24 N ?

52. Calculate the molarity of a solution that contains 1·22 g of haemoglobin (mol wt. 68300) in 165 ml of solution. [***Ans.*** $1{\cdot}08 \times 10^{-4}$M] [*W.B.J.E.* '95]

PROPERTIES OF GASES 7

7.1. Special properties of gases.

Material world is a conglomeration of energy and matter. Difference in energy leads to the transformation of matter in three different states of aggregation—solid, liquid and gases. Of these three, the gaseous state exhibits some uniform behavior which are not exhibited by the solid and liquid state. The special properties of gases are given below—

(i) **Expansibility :** Gases exhibit unlimited power of expansion. As the intermolecular forces which are acting among the gaseous molecules are very low, the distance among the molecules of a gas increases so much that the total volume of the molecule becomes negligible in comparison to the volume of the gas. The force of attraction among the molecules of a gas being very low, the gases can expand easily. This explains why a gas does not have any definite shape or volume.

(ii) **Compressibility :** As the pressure on a definite mass of a gas is increased, the intermolecular space is decreased and the molecules come closer to each other. As a result the volume of the gas decreases and the density increases.

(iii) **Gaseous pressure :** Since the intermolecular forces of attraction among the molecules are very negligible, the molecules move freely in all directions. In a gas negligible resistance is offered to the movements of its molecules. Consequently the gaseous molecules are in continuous motion and thus ceaseless hail of elastic molecules impinges on the walls of the container and the colliding molecules rebound in the gas without any decrease in their velocities. Thus the pressure exerted by the gas is due to the collisions of the gas molecules against the walls of the container.

(iv) **Effect of heat on gas :** When a definite mass of a gas is kept enclosed in a vessel and is heated, the kinetic energy i.e., the velocity of the gaseous molecules increases which strike the inner walls of the container with increased force and as a result the pressure of the gas increases. If the pressure is kept constant, the volume of the gas is increased due to the thrust of the gaseous molecules.

At constant pressure, all the gases expand to the same extent for the identical increase of temperature. The volume of a gas decreases with the increase of pressure on a gas at constant temperature. On the contrary the volume of a gas increases with the increase of temperature at constant pressure.

(v) **Gaseous diffusion :** When two or more gases which do not react with each other, are brought in contact they intermix with one another forming a homogeneous mixture. This spontaneous mixing of gases with one another is known as diffusion.

7.2. State variables.

The gaseous state of matter is expressed by state variables. Four variables—the *temperature (T), pressure (P), volume (V)* and *amount of gas in terms of moles (n)* are sufficient to define the state of a gas.

(i) **Temperature :** The temperature *(T)* of a gas is measured by thermometer. The units of temperature are degree celsius (°C) and kelvin (K).

T (in kelvin) = t°C + 273

Thus, 27°C = 273 + 27 = 300 K.

(ii) **Pressure :** Force per unit area is called pressure *(P)*. The unit of pressure is *newton per square meter* (Nm^{-2}). The other units by which pressure is expressed are *atmosphere* (atmos.), *millimeter of Hg* (mm Hg), *Pascal* (Pa) and *bar*.

$$1 \text{ bar} = 10^5 \text{ N/m}^2$$

$$1 \text{ atmos} = 76 \text{ cm Hg} = 760 \text{ mm Hg} = 101325 \text{ Pa} = 101325 \text{ Nm}^{-2}.$$

(iii) **Volume :** The volume *(V)* of a gas is expressed as *millilitre* (ml), *cubic centimeter* (cm^3), litre (L), cubic decimeter (dm^3).

$$1 \text{ ml} = 1 \text{ cm}^3 = 10^{-3} \text{ L} = 10^{-3} \text{ dm}^3 = 10^{-6} \text{ m}^3$$

(iv) **Amount of gas :** The amount or quantity *(n)* of a gas is expressed as the number of moles in a given mass of gas. It is obtained by dividing the *mass (W)* of the gas by its *molecular wt. (M)*. Thus $n = W/M$.

7.3. Volume-Pressure relation of a gas—Boyle's law.

At constant temperature and pressure a known quantity of a gas has a fixed volume. Now if the pressure of the same quantity of the gas is increased keeping the temperature constant, its volume is decreased and on lowering the pressure the volume is increased. Thus, the first relationship between the state variables was stated by Robert Boyle in 1662. This is known as Boyle's law.

- **Boyle's law :** *At constant temperature, the volume of a definite mass of a gas is inversely proportional to the pressure of the gas.*

Robert Boyle

Explanation : At constant temperature when the pressure on a gas is increased its volume is decreased. Now if the pressure on the gas is doubled, the volume will decrease to one half of its original volume at constant temperature. Again if the pressure is decreased to one half of the initial value, the volume is doubled.

Let us suppose that the volume of a gas is 20 ml at 30°C and 760 mm pressure. Now if the pressure is doubled i.e., 2 × 760 mm pressure be applied on the gas keeping the temperature constant, the volume of the resultant gas will be 20/2 = 10 ml. If the pressure is increased 4 times the initial, the volume of the gas would be 20/4 = 5 ml (Temperature is constant).

- **Mathematical interpretation of Boyle's law :**

Let the pressure of a definite mass of a gas be P and the volume be V. If the temperature be TK (Kelvin), then according to Boyle's law—

$V \propto \frac{1}{P}$ when temperature T and the mass n remain constant.

or, $V = KP^{-1}$, K is the proportionality constant.

or, $PV = K$ (constant)

i.e., *Pressure on a gas × its volume = constant.*

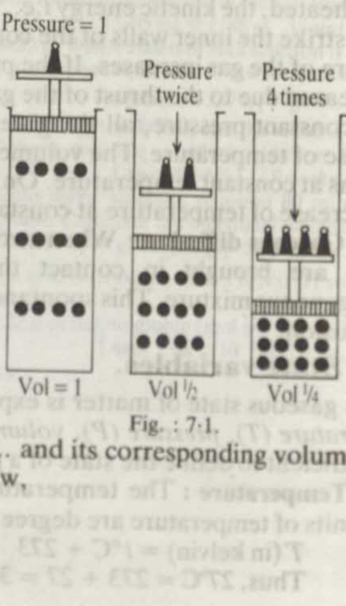


Fig. : 7·1.

At constant temperature, if the pressure on a definite mass of a gas be P_1, P_2, P_3, P_4 ..... and its corresponding volumes be V_1, V_2, V_3, V_4 ....., then according to Boyle's law,

$$P_1V_1 = P_2V_2 = P_3V_3 \text{ etc.}$$

The pressure and volume data for 0·5 mole of a gas at 300 K are given below.

P(atm)	**V(dm³)**	**P × V**	**1/P**
0·2	60	12	5
0·3	40	12	3·3
0·4	30	12	2·5
0·6	20	12	1·6

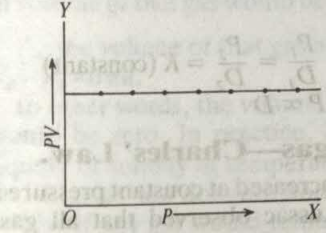


Fig. 7·2 *PV* vs *P* Graph *T* constant

(i) Now plotting *P* against *PV* a straight line should be obtained (Fig. 7·2) which is parallel to the *X*-axis. This exhibits the constancy of the product of pressure and volume of a definite mass of a gas at constant temperature. The graph shows that the product of *P* and *V* for a definite mass of a gas at a constant temperature does not depend on its pressure.

(ii) Again when pressure *(P)* of a definite mass of a gas is plotted against its volume *(V)* (Fig. 7·3) at constant temperature a rectangular *hyperbolic* graph is obtained. The graph clearly reveals that as pressure increases the volume of a given mass of gas at constant temperature decreases. If *P* is plotted against *V* at different temperatures, different *hyperbolas* are obtained as shown in the diagram where $t_2 > t_1$. Since *temperature remains constant, this type of graph is called isothermal curve.* This graph confirms the truth of Boyle's law.

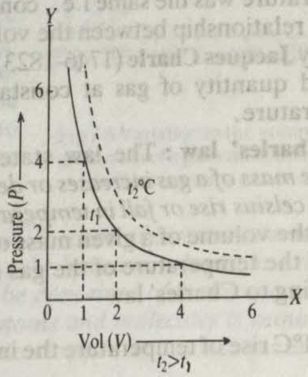


Fig. 7·3

- **Applicability of Boyle's law :**

Since *PV* = constant, a straight line parallal to curve should be obtained as mentioned earlier when *PV* is plotted against *P*. But **Regnault** and **Amagat** showed that over a wide range of pressure, particularly at high pressure the curve is not at all straight. This means that gases do not strictly obey Boyle's Law. The original data upon which Boyle based his law was rather scanty.

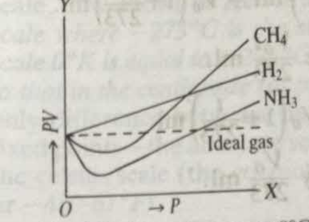


Fig. 7·4 : *PV* vs *P* curve at 0°C

The deviation of Boyle's Law is shown in the adjacent isotherm. Hydrogen and inert gases give curves which rise steadily, while other gases have decreasing trend at first. A gas which gives a straight line is regarded as an ideal gas. *Any gas which obeys Boyle's law is regarded as an ideal gas.* But there is no gas which can be regarded as an ideal gas. Hydrogen obeys Boyle's law only at low pressure.

- **Relation between pressure and density of a gas :**

Boyle's law can be used to deduce a relation between pressure and density of a gas. Let the volume of a given mass of gas at constant temperature be V_1 and V_2 at pressures P_1 and P_2 respectively.

Now applying Boyle's law $P_1V_1 = P_2V_2$

$$\text{or, } \frac{V_1}{V_2} = \frac{P_2}{P_1} \quad \cdots\cdots\cdots (1)$$

Let the mass of the given gas be M. D_1 and D_2 be the densities of the gas at pressures P_1 and P_2 respectively.

Since the mass of the gas remains constant.

$$\therefore\ D_1 = \frac{M}{V_1} \text{ and } D_2 = \frac{M}{V_2} \quad \text{or, } V_1 = \frac{M}{D_1} \text{ and } V_2 = \frac{M}{D_2}$$

Substituting the values of V_1 and V_2 in eq. (1),

$$\frac{M/D_1}{M/D_2} = \frac{P_2}{P_1} \quad \text{or, } \frac{D_2}{D_1} = \frac{P_2}{P_1} \quad \text{or, } \frac{P_1}{D_1} = \frac{P_2}{D_2} = K \text{ (constant)}$$

$$\text{or, } P/D = K \quad \text{or, } P = KD, \text{ i.e., } P \propto D$$

7.4. Temperature-volume relation of a gas—Charles' Law.

When the temperature of a fixed mass of a gas is increased at constant pressure its volume will also increase and vice-versa. Gay Lussac observed that all gases behaved similarly and that the change in volume of all gases for a given rise of temperature was the same i.e., constant and independent of the nature of the gas.

The relationship between the volume and temperature of a gas was discovered in 1787 by **Jacques Charle** (1746-1823), a French scientist. He found that the volume of a fixed quantity of gas at constant pressure increases in a linear fashion with temperature.

- **Charles' law** : The law states that—*At constant pressure, the volume of a definite mass of a gas increases or decreases by 1/273 part of its volume at 0°C, for each degree celsius rise or fall in temperature.*

Let the volume of a given mass of a gas at constant pressure and at 0°C be V_0 ml. Now if the temperature of the gas is increased keeping the pressure constant, then according to Charles' law—

For 1°C rise of temperature the increase in volume will be $\frac{V_0}{273}$ ml.

$\therefore$ At 1°C the volume of the gas will be $\left(V_0 + \frac{V_0}{273}\right)$ ml $= V_0\left(1 + \frac{1}{273}\right)$ ml.

Again for the increase of 20°C the increase in volume will be $\frac{20 \times V_0}{273}$ ml.

$\therefore$ At 20°C the volume of the gas will be $\left(V_0 + \frac{20 \times V_0}{273}\right)$ ml $= V_0\left(1 + \frac{20}{273}\right)$ ml.

For the increase of t°C the increase of volume will be $\frac{V_0 t}{273}$ ml.

$\therefore$ At t°C the volume of the gas $= \left(V_0 + \frac{V_0 t}{273}\right)$ ml $= V_0\left(1 + \frac{t}{273}\right)$ ml.

Again for a decrease of 1°C, the volume decreases by $\frac{V_0}{273}$ ml.

$\therefore$ At -1°C the volume of the gas $= \left(V_0 - \frac{V_0}{273}\right)$ ml $= V_0\left(1 - \frac{1}{273}\right)$ ml.

Thus, for a decrease of t°C the volume of the gas decreases by $\frac{V_0 t}{273}$ ml.

$\therefore$ At $-t$°C the volume of the gas $= \left(V_0 - \frac{V_0 t}{273}\right)$ ml $= V_0\left(1 - \frac{t}{273}\right)$ ml.

or, in other words, mathematical expression of Charles' law is $V_t = V_0\left(1+\frac{t}{273}\right)$

where V_t = volume of the gas at t°C and
V_0 = " " " " at 0°C

7.5. Absolute temperature and Absolute zero.

Now it is clear from the above discussion that at constant pressure if V_0 ml of any gas is subjected to a temperature of −273°C then following Charles' law the decrease in volume of that gas would be $\frac{V_0 \times 273}{273} = V_0$ ml

$\therefore$ the volume of that gas at −273°C would be $V_0 - V_0 = 0$ ml.

In other words, the volume of a gas at −273°C would be zero. In practice, however, all gases liquefy or solidify at temperature above −273°C and Charles' law does not hold good to liquids or solids. If any gas would remain in gaseous state then at −273°C its volume would be zero. Hence volumes of gases cannot, therefore, be measured right down to −273°C but if the volume of a given mass of a gas is measured at different temperatures and the plots are extrapolated, it can be shown theoretically that the gas would have no volume if its temperature is brought down to −273°C (Fig 7·5).

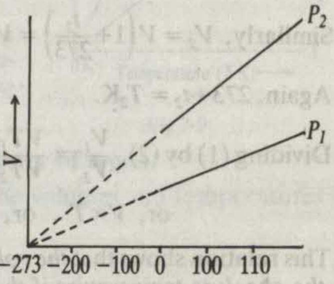


Fig 7·5 Variation in the volume of a given mass of a gas with temperature in °C at constant pressure

- **Absolute zero :** *According to Charles' law, at constant pressure, the temperature (−273°C), at which, theoretically a gas would have no volume, is known as absolute zero. A temperature below this cannot be conceived of in the universe. It is the temperature at which the kinetic energy of atoms and molecules is minimal.* At absolute zero, the movements of molecules are stopped and consequently their average kinetic energy would be zero.

- **Absolute scale of temperature :**

Absolute zero provides the starting point for a scale of temperature known as Absolute scale. In 1848, **William Thomson** (1824-1907), a British physicist whose title was **Lord Kelvin** proposed the idea of an absolute scale, now known as *Kelvin scale. It is a thermometric scale where −273°C is the starting point i.e., on this scale 0°K is equal to −273°C and each degree is equal to that in the centigrade (at present celsius) scale.* The only difference between the two lies in their lower fixed points—the absolute scale (*K*) starts at −273° of the celsius scale (the correct value being −273·15°C or −459·67°*F*).

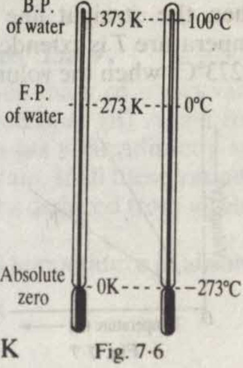


Fig. 7·6

In general K = °C+273
thus 10°C = 10+273 = 283K
In absolute scale 0 K = −273°C = −459·67°F
Boiling point of water = 100°C = 100+273 = 373K
−10°C = 273−10 = 263K
−273°C = 273−273 = 0 K

7.6. Charles' Law and Absolute scale of temperature—alternative statement of Charles' law.

Let at constant pressure and at 0°C the volume of a fixed mass of a gas be V ml. V_1 and V_2 be respectively the volumes of the same mass of gas at temperatures t_1°C and t_2°C.

According to Charle's Law,—

$$V_1 = V\left(1+\frac{t_1}{273}\right) = V\left(\frac{273+t_1}{273}\right)$$

Now, $273+t_1 = T_1$K. $\quad\therefore\ V_1 = V\times\frac{T_1}{273}$ ……… (1)

Similarly, $V_2 = V\left(1+\frac{t_2}{273}\right) = V\left(\frac{273+t_2}{273}\right)$

Again, $273+t_2 = T_2$K. $\quad\therefore\ V_1 = V\times\frac{T_2}{273}$ ……… (2)

Dividing (1) by (2), $\frac{V_1}{V_2} = \frac{VT_1/273}{VT_2/273} = \frac{T_1}{T_2}$ or, $\frac{V_1}{V_2} = \frac{T_1}{T_2}$

or, $V \propto T$ or, $\frac{V}{T}$ is constant. (K)

This relation shows that *the volume of a given mass of a gas is directly proportional to the absolute temperature if the pressure remains constant.* This is an alternative statement of Charles' law.

The value of the constant K depends on the mass and pressure of the gas.

Volume-temperature data for 0·2 mole of a gas at 1 atm pressure are given below—

T in Kelvin	V in litre	V/T	
200	3·2	0·016	Constant
300	4·8	0·016	
400	6·4	0·016	
500	8·0	0·016	

If the volumes of a given mass of gas are plotted against absolute temperatures at constant pressure, the plots will give a straight line which confirms that gas obeys Charles' law. *Such a straight line is called isobar as the pressure remains constant.* When the straight line representing the change in volume (V) with absolute temperature T is extended to meet the X axis. it is found that it meets the X axis at 0 K (−273°C) when the volume of the gas is zero.

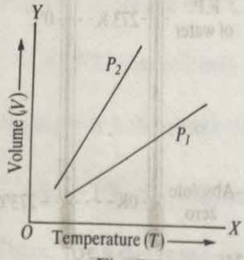


Fig. 7·7

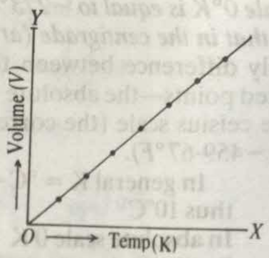


Fig 7·8

- **Law of pressure :** *If the volume of a given mass of a gas remains constant, the pressure of the gas increases or decreases by 1/273 part of its pressure at 0°C for each degree celsius rise or fall in temperature.*

The above statement leads the conclusion that *the pressure of a given mass of gas is directly proportional to the absolute temperature, if the volume of the gas remains constant.*

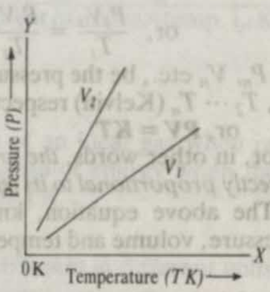


Fig 7·9

$$P \propto T \text{ or, } \quad \frac{P}{T} = \text{constant} \quad \text{ or, } \frac{P_1}{P_2} = \frac{T_1}{T_2}$$

Let the pressure of a fixed volume of gas at T_1K be P_1 and at T_2K be P_2 then from the above law,

$\frac{P_1}{P_2} = \frac{T_1}{T_2}$ Mass and volume of the gas being constant.

Linear curves will be obtained when P_1, P_2, P_3 etc., be plotted against corresponding absolute temperatures T_1, T_2, T_3 etc. The two curves are shown where $V_1 > V_2$ (Fig 7·9)

• Relation between temperature and density of a gas.

At constant pressure, let V_1, T_1 and V_2, T_2 be the volumes and temperatures in absolute scale, of a fixed mass of gas.

From Charles' Law, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ or, $\frac{V_1}{V_2} = \frac{T_1}{T_2}$ ………… (1)

Let M be the mass of the gas then—

$$V_1 = \frac{M}{D_1}; \qquad V_2 = \frac{M}{D_2}$$

D_1 and D_2 being the densities of the gas at temperatures T_1 and T_2.

Substituting the value of V_1 and V_2 in equation (1),

$$\frac{\frac{M}{D_1}}{\frac{M}{D_2}} = \frac{T_1}{T_2} \quad \text{or,} \quad \frac{D_2}{D_1} = \frac{T_1}{T_2}$$

$$\text{or,} \quad D_1T_1 = D_2T_2 \quad \text{or,} \quad DT = \text{constant } (K)$$

$$\text{or,} \quad D = \frac{K}{T} \quad \text{or,} \quad D \propto \frac{1}{T}$$

Thus, *pressure remaining constant, the density of a fixed mass of a gas is inversely proportional to its temperature in absolute scale.*

7.7. Combination of Boyle's Law and Charles' Law.

(i) From *Boyle's Law* we know that volume of a given mass of a gas varies inversely with the pressure when temperature remains constant. (ii) Again from *Charles' Law* we learn that volume of a given mass of a gas varies directly with temperature in absolute scale when pressure remains constant. If all these variables change simultaneously then the relation among them can be deduced from algebric consideration.

Let *P*, *V* and *T* be respectively the pressure, volume and temperature in absolute scale (K) of a fixed mass of a gas, then

$V \propto \frac{1}{P}$ when T is constant (Boyle's Law)

Again $V \propto T$ when P is constant (Charles' Law)

$\therefore \quad V \propto \frac{T}{P}$ when both P and T vary or, $V = K.\frac{T}{P}$ where K = constant or, $\frac{PV}{T} = \text{constant} = K$

or, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} \ldots\ldots\ldots = \frac{P_nV_n}{T_n} = K$, (where P_1, V_1 ; P_2, V_2 ; $\cdots$ P_n, V_n etc., be the pressures and volumes of a fixed mass of gas at temperatures T_1, $T_2 \cdots T_n$ (Kelvin) respectively.

or, $PV = KT$

or, in other words, *the product of pressure and volume of a fixed mass of gas is directly proportional to its temperature in absolute scale.*

The above equation, known as *gas equation* which gives a relation among pressure, volume and temperature of a given mass of a gas.

- **Molar Gas Constant :**

It is obvious from the equation $PV = KT$ that at constant temperature and pressure the value of the constant K is proportional to the quantity of gas. We know from Avogadro's Law that, *the molar volume of all gases is the same under the same conditions of temperature and pressure and is equal to 22·4 litre at N.T.P. Hence the numerical value of K is the same for 1 gram mole of all gases.* Therefore if 1 gram mole of any gas is considered, K is generally denoted by a symbol R and the gas equation then becomes $PV = RT$.

R=Molar gas constant. The value of R does not depend upon the nature of the gas. Its value is constant for all gases, independent of the nature of the gas and hence called **Universal gas constant.** Here V is the volume of 1 mole of any gas and hence called molar volume. The equation $PV = RT$ is called *equation of state* and is applicable for all ideal gases i.e., those gases which obey Boyle's law and Charles' law and it is applicable for 1 mole of an ideal gas.

- **Ideal gas equation ·**

The Boyle's law, Charles's law and Avogadro's law on combination give ideal gas equation. From Boyle's law, we get $V \propto P^{-1}$ when T and n (number of moles) are constants. From Charles' law, we get $V \propto T$ when P and n are constants and from Avogadro's law $V \propto n$ when T and P remain constant.

$\therefore\ V \propto P^{-1}.\ T.\ n$ or, $V = R\,P^{-1}\,T\,n$

or, $PV = nRT$.

This is called ideal gas equation.

Ideal gas : *Ideal gases are those which obey Boyle's Law and Charles' Law* i.e., the ideal gases are those which obey the above $PV = nRT$ equation and *the gases which do not obey this equation are called Real gases.* Unfortunately no gases are known which obey this equation and the concept of Ideal gas is really a theoretical one.

- **Dimension of molar gas constant R :**

The dimension of R can be evaluated as follows :—

$PV = nRT$

$$R = \frac{PV}{nT}$$

$$R = \frac{\text{Pressure} \times \text{Volume}}{\text{Number of moles} \times \text{Temperature in K}}$$

Now Pressure $= \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{Length})^2}$ and Volume $= (\text{Length})^3$

$$\therefore\ R=\frac{\dfrac{\text{Force}}{(\text{Length})^2}\times(\text{Length})^3}{\text{Number of moles}\times\text{Temperature in K}}=\frac{\text{Force}\times\text{Length}}{\text{Number of moles}\times\text{temp. in K}}$$

$$=\frac{\text{Work done}}{\text{temp. in K}}\text{ per mole}$$

R=Work done (i.e., Energy) per K per mole

Thus R denotes magnitude of work done by 1 mole of an ideal gas when its temperature is increased by 1 K or it expresses the change of energy when the temperature of 1 mole of a gas is increased or decreased by 1 K.

• The Numerical value of *R* :

Although R is an universal constant, the value of R is different in different units because work done i.e., energy is expressed in different units.

(1) *In C.G.S. and S.I. Unit.*

The unit of work on C.G.S. unit is *ergs per Kelvin per mole,* 1 erg being the work done when a force of 1 dyne acts through a distance of 1 cm.

A pressure of 1 atmosphere=76×13·6×981 dynes per sq. cm.

where normal pressure = pressure of 76 cm of Hg column, g = 981 cm/sec^2

Density of Hg at 0°C=13·6 g/ml.

Experiments show that 1 gram mole of any gas at N.T.P. occupy 22·4 litre or 22400 ml.

$$\therefore\ R=\frac{PV}{T}=\frac{76\times13{\cdot}6\times981\times22400}{273}\text{ erg per Kelvin per mole}$$

$$=8{\cdot}314\times10^7\text{ erg per Kelvin per mole}$$

$$=8{\cdot}314\text{ Joule per Kelvin per mole}=8{\cdot}314\text{ JK}^{-1}\text{mole}^{-1}$$

(2) *In litre-atmosphere—*

P=1 atmosphere, V=22·4 litre T=273K

$$R=\frac{PV}{T}=\frac{1\times22{\cdot}4}{273}=0{\cdot}082\text{ litre-atmosphere per Kelvin per mole.}$$

(3) *In Calorie—*

R in C.G.S. unit=8·314×10^7 erg per Kelvin per mole

Again 1 calorie=4·183×10^7 erg

$$\therefore\ R=\frac{8{\cdot}314\times10^7}{4{\cdot}183\times10^7}=1{\cdot}987\text{ calories per Kelvin per mole.}$$

$$\simeq2\text{ cals per Kelvin per mole.}$$

• Use of Gas Equation :

(1) For 1 mole of gas $PV=RT$

for n moles of gas $PV=nRT$

From the above equations any of the four quantities namely P, V, n and T can be evaluated if 3 others are known. R is constant but its correct unit must be used otherwise results will be erroneous.

Thus to calculate the volume occupied by two moles of a gas say nitrogen at 0°C and 2 atmosphere pressure, the unit of R must in litre-atmos. per Kelvin per mole.

$$\text{or, }V=\frac{nRT}{P}=\frac{2\text{ moles}\times0{\cdot}082\text{ lit-atmos K}^{-1}\text{ mole}^{-1}\times273\text{ K}}{2\text{ atmos}}$$

$$=22{\cdot}4\text{ litre (all other units are cancelled)}$$

(2) *The molecular weight of any gas can be calculated by applying the equation of state*

Let the weight of the gas=w g, Molecular weight of the gas=M

$\therefore$ Number of moles of the gas$=\frac{w}{M}$, $n=\frac{w}{M}$

$$PV=nRT \text{ or, } PV=\frac{w}{M}RT$$

Hence Molecular weight *(M)* of the gas can be found out from a knowledge of *P*, *V*, *w*, *R* and *T*

[**N.B.** : Check the unit of *M* it will be gram per mole]

• Effect of pressure and temperature on the density of gas—Relation among them.

From Boyle's law we know temperature remaining constant volume of a given mass of gas is inversely proportional to its density.

$$V \propto \frac{1}{D} \quad V=\text{Volume}, D=\text{Density}$$

$$\text{or, } V=\frac{K}{D}, \text{ or, } DV=K$$

$$\text{or, } D_1V_1=D_2V_2=K$$

$$\text{or, } \frac{D_1}{D_2}=\frac{V_2}{V_1} \cdots\cdots\cdots\text{(i)}$$

Combination of Charles's Law and Boyles' Law gives

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2} \text{ or, } \frac{P_1T_2}{P_2T_1}=\frac{V_2}{V_1} \cdots\cdots\cdots\text{(ii)}$$

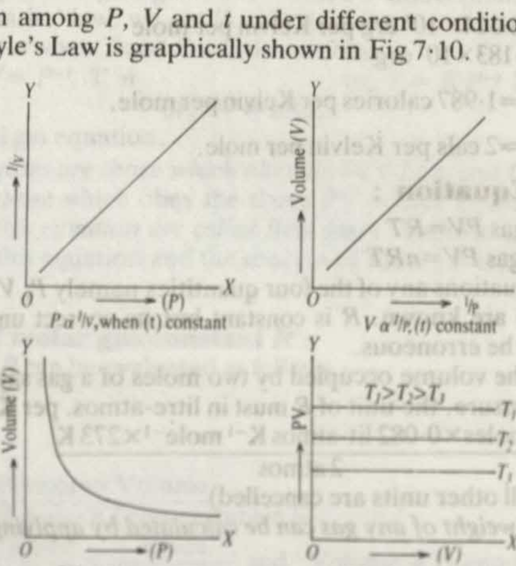
From equation (i) and (ii),

$$\frac{D_1}{D_2}=\frac{P_1T_2}{P_2T_1} \text{ or, } \frac{D_1T_1}{P_1}=\frac{D_2T_2}{P_2}=\text{constant} \cdots\cdots\cdots\text{(iii)}$$

Equation (iii) denotes the combined effect of pressure and temperature on the density of gases i.e., how density of a gas is changed when both pressure and temperature change simultaneously.

• Different graphs relating *P*, *V* and *T* of gases :

(i) The relation among *P*, *V* and *t* under different conditions obtained by the application of Boyle's Law is graphically shown in Fig 7·10.



$P \propto 1/v$, when (t) constant

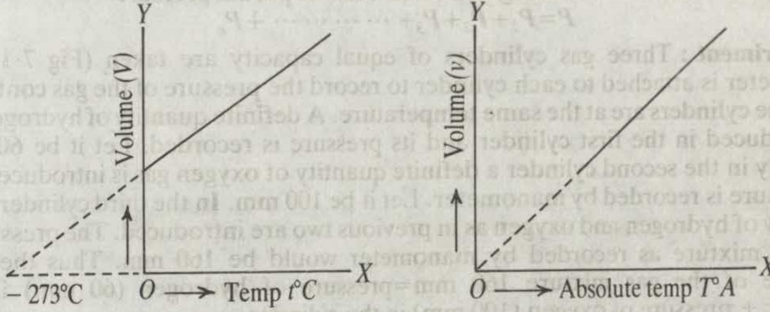
$V \propto 1/P$, (t) constant

$PV = K_1(t)$ constant

$PV = K_1(t)$ constant

Fig 7·10

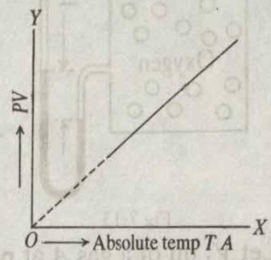
(ii) Similarly the Fig 7·11 is the graphical representation of P, V and T relation as obtained from Charles's Law



$V \propto t$, P constant $\qquad$ $V \propto T$, P constant

Fig 7·11

(iii) The results obtained by applying the equation of state are graphically shown in Fig 7·12



$$\frac{PV}{T} = K$$

Fig 7·12

7.8. Partial pressure and Dalton's law of partial pressure.

Boyle's law explained the effect of pressure on the volume of a fixed mass of a gas at constant temperature. Dalton tried to establish a relation between the total pressure of a mixture of several non-reacting gases and the individual pressures of the constituent gases at constant temperature and the law he enunciated is commonly called *Dalton's law of partial pressure.*

Dalton's Law of Partial Pressure : *At constant temperature, when two or more gases or vapours which do not react chemically with one another are mixed together in a vessel of fixed volume, the total pressure of the mixture of gases or vapours is the sum of the partial pressure of each of the constituent gases or vapours.*

In other words the total pressure of non-reacting gas mixture at constant temperature and volume=sum of the partial pressure of each of the constituent gases.

$$\text{or, } P = p_1 + p_2 + p_3 \cdots\cdots$$

where p_1, p_2 and p_3 are the partial pressures of gases say A, B, C etc., (at the same temp.) and total pressure of these gases contained in a flask=P.

Partial Pressure : *The partial pressure of any constituent gas or vapour in a mixture is defined as the pressure which the constituent would exert if it alone had occupied the space in which the mixture of gases or vapours is contained, temperature in both the cases remains constant.*

Explanation : Let us take several gases of pressures $P_1, P_2, P_3 \ldots\ldots\ldots\ldots P_n$ at same temperature and volume and if the total pressure of them at the same temperature and volume be P then according to Dalton's law of partial pressure.

$$P = P_1 + P_2 + P_3 + \cdots\cdots\cdots\cdots + P_n$$

Experiment : Three gas cylinders of equal capacity are taken (Fig 7·13). A manometer is attached to each cylinder to record the pressure of the gas contained in it. The cylinders are at the same temperature. A definite quantity of hydrogen gas is introduced in the first cylinder and its pressure is recorded. Let it be 60 mm. Similarly in the second cylinder a definite quantity of oxygen gas is introduced and its pressure is recorded by manometer. Let it be 100 mm. In the third cylinder same quantity of hydrogen and oxygen as in previous two are introduced. The pressure of the gas mixture as recorded by manometer would be 160 mm. Thus the total pressure of the gas mixture 160 mm = pressure of hydrogen (60 mm) in the cylinder + pressure of oxygen (100 mm) in the cylinder.

The experiment confirms the correctness of Dalton's law of partial pressure.

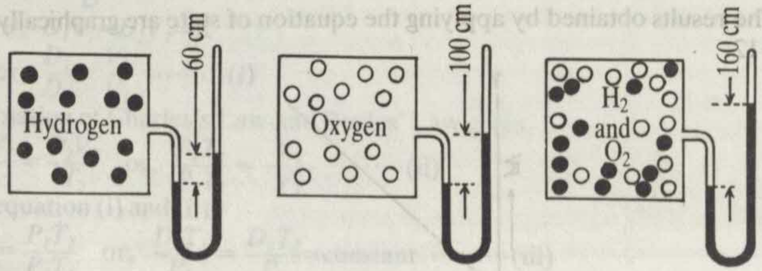


Fig 7·13

Mathematical deduction : Let V_1 ml of a gas A at pressure P_1 be confined in the vessel I (Fig 7·14). The other vessel of volume V_2 is empty and the two vessels are connected by a glass tube having a stop-cock. The whole apparatus is under Isothermal condition. On opening the stop-cock, V_1 ml of the gas A at pressure P_1 will also fill the second vessel (II). As a result the volume of the gas becomes $(V_1 + V_2)$ ml. Let P_A be the pressure of this mixed volume of gas A.

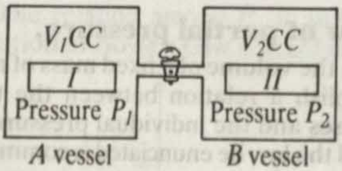


Fig 7·14

Applying Boyle's Law,

$$P_1 \times V_1 = P_A (V_1 + V_2)$$

$$\text{or, } P_A = \frac{P_1V_1}{V_1 + V_2}$$

P_A = Partial pressure of V_1 ml gas at that temperature

Again let us consider the vessel I is empty. The vessel II contains V_2 ml of gas B at pressure P_2. On opening the stop-cock the vessel I is completely filled with V_2 ml of the gas B at pressure P_2. The temperature, as in the previous experiment, remains constant. The volume of the gas B will be increased to $(V_1 + V_2)$ ml. Let the pressure of this mixed volume be P_B

Applying Boyle's Law :

$$P_2V_2 = P_B (V_1 + V_2)$$

$$\text{or, } P_B = \frac{P_2V_2}{V_1 + V_2}$$

P_B = Partial pressure of V_2 ml gas at constant temperature.

Now the two gases in the two vessel I & II are allowed to mix. Let P = total pressure of the mixture of gas.

From Dalton's Law of Partial pressure

$$\begin{aligned} P &= P_A + P_B \\ P &= \frac{P_1V_1}{V_1+V_2} + \frac{P_2V_2}{V_1+V_2} \\ or,\ P &= \frac{P_1V_1+P_2V_2}{V_1+V_2} \end{aligned}$$

- **Pressure of gas collected on water—aqueous tension :**

Whenever a water insoluble gas is collected over water, the gas becomes saturated with water vapour at room temperature. The volume of the gas is measured in Eudiometer tube by placing it into a tall jar full of water. The surface of water inside and outside the tube is then brought to the same level by holding it with a clamp or a piece of paper, and the volume of the gas inside the tube is noted. Under this experimental condition the pressure of moist gas inside the tube is equal to the atmospheric pressure at the room temperature.

Let p_1 be pressure of dry gas at the temperature of the room, f be the vapour pressure of water (Aqueous tension) at that temperature and P be the atmospheric pressure.

According to Dalton's Law of Partial Pressure,

$$P = p_1 + f$$

$$\text{or, } p_1 = P - f$$

Pressure of dry gas = Atmospheric pressure − Aqueous tension.

7.9. Relation between partial pressure and mole fraction.

Let $n_1, n_2, n_3 \cdots\cdots n_n$ are the respective moles of several non reacting gases in a vessel of volume V at temperature T. Let the total pressure of the gas mixture be P. Again $P_1, P_2, P_3 \cdots\cdots P_n$ = the respective partial pressure of the gases i.e., the pressures which each gas would exert if allowed to occupy the entire volume V.

Applying gas law equation to each case,

$$\begin{aligned} P_1V &= n_1RT \cdots\cdots\cdots \text{(i)} \\ P_2V &= n_2RT \cdots\cdots\cdots \text{(ii)} \\ P_3V &= n_3RT \cdots\cdots\cdots \text{(iii)} \\ P_nV &= n_nRT \cdots\cdots\cdots \text{(iv)} \end{aligned}$$

From Dalton's Law of Partial Pressure,

$$P = P_1 + P_2 + P_3 + \cdots\cdots + P_n$$

Let the total number of moles of the gases be n

$$\therefore n = n_1 + n_2 + n_3 + \cdots\cdots + n_n$$

$\therefore$ The gas equation when applied to the mixture of gases

$$(P_1 + P_2 + P_3 + \cdots\cdots + P_n)V = (n_1 + n_2 + n_3 + \cdots\cdots + n_n)RT$$

$$\text{or } PV = nRT \cdots\cdots\cdots \text{(v)}$$

Dividing (i) by (v),

$$\frac{P_1}{P} = \frac{n_1}{n}$$

$$\text{or, } P_1 = \frac{n_1}{n}P \cdots\cdots\cdots \text{(vi)}$$

Similarly by dividing (ii), (iii) & (iv) respectively by (v) we get,

$$P_2 = \frac{n_2}{n} P \cdots\cdots\cdots \text{(vii)}$$

$$P_3 = \frac{n_3}{n} P \cdots\cdots\cdots \text{(viii)}$$

$$P_n = \frac{n_n}{n} P \cdots\cdots\cdots \text{(ix)}$$

The term $\frac{n_1}{n}$, $\frac{n_2}{n}$, $\frac{n_3}{n}$ etc., is called mole fraction.

Mole fraction : *The ratio of the number of moles of a component present, to the total number of moles in the system is called the mole fraction of the component. It is a way of expressing the concentration of a component in terms of mole.*

Substituting $\frac{n_1}{n} = m_1$, $\frac{n_2}{n} = m_2$, $\frac{n_3}{n} = m_3 \cdots\cdots\cdots \frac{m_n}{n} = m_n$

the equations (vi), (vii), (viii), (ix) can be reduced to

$$P_1 = m_1 P \; ; \quad P_2 = m_2 P \; ; \quad P_3 = m_3 P \; ; \quad P_n = m_n P$$

or, *Partial pressure of a gas in a mixture, is equal to the product of its mole fraction × total pressure of the gas mixture.*

Partial pressure of a gas in a mixture=Its mole fraction × total pressure

Again it can be shown that the sum total of mole fraction of all the components in the system would be unity.

$$m_1 = \frac{n_1}{n} = \frac{n_1}{n_1+n_2+n_3+\cdots\cdots\cdots+n_n}$$

$$m_2 = \frac{n_2}{n} = \frac{n_2}{n_1+n_2+n_3+\cdots\cdots\cdots+n_n}$$

$$m_3 = \frac{n_3}{n} = \frac{n_3}{n_1+n_2+n_3+\cdots\cdots\cdots+n_n}$$

$$m_n = \frac{n_n}{n} = \frac{n_n}{n_1+n_2+n_3+\cdots\cdots\cdots+n_n}$$

On adding, $m_1+m_2+m_3+\cdots\cdots\cdots+m_n = \frac{n_1}{n} + \frac{n_2}{n} + \frac{n_3}{n} + \cdots\cdots + \frac{n_n}{n}$

$$= \frac{n_1+n_2+n_3+\cdots\cdots+n_n}{n} = \frac{n_1+n_2+n_3+\cdots\cdots+n_n}{n_1+n_2+n_3+\cdots\cdots+n_n} = 1$$

7.10. Amagat's Law of Partial Volume.

Amagat's Law of partial volume states "*At constant temperature and pressure, the total volume occupied by a mixture of two or more non-reacting gases or vapours is equal to the sum of the partial volumes of the constituent of the gas mixture.*"

or, mathematically, $V = v_1+v_2+v_3+\cdots\cdots+v_n$

where v_1, $v_2 \cdots\cdots$ etc., be the partial volumes and V is the total volume of the gas mixture.

Partial volume is the volume occupied by a constituent gas in a mixture at pressure equal to that of the mixture, the temperature remaining constant. It can be shown mathematically.

Partial volume = Its mole fraction × Total volume of the gas mixture

Applying gas equation,

$$\left.\begin{aligned} v_1 &= \frac{n_1}{P}RT \\ v_2 &= \frac{n_2}{P}RT \\ v_3 &= \frac{n_3}{P}RT \\ v_n &= \frac{n_n}{P}RT \end{aligned}\right\} \cdots\cdots\cdots(1)$$

Applying Amagat's Law of Partial volume.

$$\begin{aligned} V &= v_1+v_2+v_3+\cdots\cdots\cdots+v_n \\ &= \frac{n_1}{P}RT+\frac{n_2}{P}RT+\frac{n_3}{P}RT+\cdots+\frac{n_n}{P}RT \\ &= (n_1+n_2+n_3+\cdots\cdots+n_n)\frac{RT}{P} \end{aligned}$$

Let N=total number of moles $= n_1+n_2+n_3+\cdots\cdots+n_n$

$$\therefore V=N\cdot\frac{RT}{P}\cdots\cdots\cdots(2)$$

Dividing (1) by (2),

$$\frac{v_1}{V}=\frac{n_1}{N} \qquad \text{or, } v_1=\frac{n_1}{N}\cdot V$$

Similarly $v_2=\frac{n_2}{N}V$; $v_3=\frac{n_3}{N}\cdot V\cdots\cdots$ $v_n=\frac{n_n}{N}\cdot V$

Since $\frac{n}{N}$ denotes mole fraction, the partial volume of a component of a gas mixture is equal to its mole fraction × total volume of the gas mixtures.

- **Kinetic theory of gases :**

The kinetic theory of gases correlates the macroscopic properties (e.g., V, T, P etc.) of a gas with its microscopic properties (e.g., *velocity, momentum of each molecule*). **Clausius, Boltzmann, Maxwell** and others have contributed towards the development of this theory.

Postulates of kinetic theory of gases :

(i) A gas is composed of a large number of minute, discrete, spherical particles of identical mass and size. The particles are called the molecules.

(ii) The volume occupied by the gaseous molecules is negligibly small as compared to the total volume occupied by the gas.

(iii) There being no intermolecular forces of attraction or repulsion between the molecules, they are in a continuous random movement in all possible directions and they move in a straight line.

(iv) While moving, the molecules collide against each other and with the walls of the container. During these collisions they change their directions of motion without any loss in their kinetic energy i.e., the collisions are perfectly elastic.

(v) The pressure exerted by the gas is due to the collisions of the gas molecules against the walls of the container. The larger the number of collisions, the greater is the pressure of the gas.

(vi) The average kinetic energy of a gas molecule is directly proportional to the absolute temperature of the gas.

(vii) The pressure exerted by the gas does not depend on the gravitational force.

- **Velocity of the gas molecules :**

All the molecules in a gas do not have the same velocity. The velocity of a particular molecule is always changing its direction and magnitude due to collisions. If at any instant n individual molecules have velocities $C_1, C_2, C_3, C_4 \cdots C_n$, (a) the arithmetic mean of the individual velocities of the molecules is called the **average velocity** (C_A).

$$C_A = \frac{C_1+C_2+C_4+C_4+\cdots\cdots+C_n}{n}$$

(b) **The root mean square velocity** (R.M.S.V) (C) is the square root of the mean of the squares of individual velocities of the gas molecules.

$$C = \sqrt{\frac{c_1^2+c_2^2+c_3^2+c_4^2+\cdots\cdots+c_n^2}{n}}$$

It has been found that $C \simeq 1{\cdot}085\ C_A$

- **Deductions from kinetic theory of gases :**

(1) **Kinetic theory and pressure of the gas :** The pressure exerted by a gas is equal to the force per unit area. The pressure exerted by the gas is due to the collisons of the molecules of the gas with the walls of the container. The pressure exerted by the gas is expressed by the following equation.

$P = mNC^2/3V$ where, P=pressure exerted by the gas, V=the volume of the gas, N=number of molecules present in volume V, m=mass of a molecule, C=root mean square velocity.

The equation $P = mNC^2/3V$ is known as *kinetic gas equation.*

(2) **The kinetic energy and temperature of a gas :**

We know that kinetic gas equation is $PV = \frac{1}{3} m N C^2$. In this equation, mN=total mass of the gas=M.

$\therefore\ PV = \frac{1}{3} MC^2$ or, $PV = \frac{2}{3} \cdot \frac{1}{2} MC^2$

but $1/2\ MC^2$=the average kinetic energy of the gas.

For one mole of an ideal gas, $PV = RT$. Putting the value of PV, we get $\frac{2}{3} \cdot \frac{1}{2} MC^2 = RT$.

Now M=molecular wt. of the gas in this equation.

$\frac{1}{2} MC^2$ is the kinetic energy E_k for one mole of the gas

$$\text{or, } \frac{2}{3} E_k = RT \qquad \text{or, } E_k = \frac{3RT}{2}$$

Since R is constant $\quad E_k \propto T$.

Now Kinetic energy E_k for one mole $= \frac{3RT}{2}$

$\therefore$ Kinetic energy for n moles $= \frac{3nRT}{2}$

As one mole of a gas contains Avogadro's number N_A i.e., $6{\cdot}023 \times 10^{23}$ molecules.

$\therefore$ Kinetic energy E_K of 1 molecule $= \frac{3RT}{2 \times 6{\cdot}023 \times 10^{23}}$

Thus the average kinetic energy of a gas molecule is proportional to the absolute temperature of the gas. At a particular temperature the kinetic energy of a molecule of any gas will be the same.

(3) **Kinetic equation and Boyle's Law :**

From Boyle's law we get PV=Constant

From kinetic equation we get $PV = \frac{1}{3}mNC^2$

$$\text{or, } PV = \frac{2}{3}N.\frac{1}{2}mC^2$$

Now for a fixed amount of gas N is constant. Hence for a fixed amount of gas and at a constant temperature $2/3\ N.\ 1/2\ mC^2$ is constant.

$\therefore$ PV=Constant and this is Boyle's law.

(4) **Charle's law :**

The kinetic gas equation is $PV = \frac{1}{3}mNC^2$

or, $PV = \frac{1}{3}MC^2$ where M = mass of the gas.

or, $V = \dfrac{MC^2}{3P} = \dfrac{2}{3P} \times \frac{1}{2}MC^2$

At constant pressure $\dfrac{2}{3P}$ is constant = K_1, say

Again $\frac{1}{2}MC^2 \propto T$, as $\frac{1}{2}MC^2$ = the kinetic energy of the gas.

i.e., $\frac{1}{2}MC^2 = K_2T$. K_2 is constant.

$\therefore$ $V = K_1.K_2T.$ or, $V/T = K_1.K_2 = K$ constant.

i.e., $V \propto T$. This is Charles' law.

(5) **Avogadro's Law :** Avogadro's law states that under the same conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules.

Let the two gases A and B of equal volumes are taken at the same temperature and pressure. Let the number of molecules in A and B are N_A and N_B respectively. From kinetic gas equation for equal volumes of two gases at a fixed temperature.

$$PV = \frac{1}{3}M_AN_AC_1^2 = \frac{1}{3}M_BN_BC_2^2$$

$$\text{or, } \frac{2}{3}N_A\frac{1}{2}M_AC_1^2 = \frac{2}{3}N_B\cdot\frac{1}{2}M_BC_2^2 \ldots\ldots \text{(i)}$$

where M_A, N_A and C_1 represent the *mass, number* and *r.m.s. velocity of the* molecules of gas A and M_B, N_B and C_2 represent the *mass, number* and *r.m.s. velocity* of the molecules of gas B.

At a given temperature the average kinetic energy of a molecule is constant.

$\therefore$ $1/2\ M_AC_1^2 = 1/2\ M_BC_2^2$.

$\therefore$ From equation (1) we get, $2/3\ N_A = 2/3\ N_B$

or, $N_A = N_B$ i.e., the number of molecules in gas A is equal to the number of molecules in gas B. This is avogadro's law.

(6) **Gas equations :**

From the kinetic gas eq. $PV = \frac{1}{3}mNC^2$

Now mN = total mass of the gas = M For 1 mole M = Mol. wt.

$\therefore$ $PV = \frac{1}{3}MC^2$ when M = mol. wt. of the gas or, $PV = \frac{2}{3}\cdot\frac{1}{2}MC^2$.

Then $\frac{1}{2}MC^2$ is the kinetic energy E_k of one mole of the gas.

Now E_k is directly proportional to the absolute temperature.

or, $E_k \propto T$, or, $E_k = K_1 T$, K_1 constant.

$$\therefore\ PV = \frac{2}{3}E_k = \frac{2}{3}K_1 T.$$

$$\text{or, } PV \propto T\ \therefore\ \frac{PV}{T} = K \text{ constant}$$

The value of K depends on the mass of the gas.

For one mole of an ideal gas K is expressed as R.

Hence, $\frac{PV}{T} = R$ or, $PV = RT$. For n moles $PV = nRT$. This is ideal gas equation.

7.11. Diffusion of gases.

When two or more non-reacting gases are brought in contact, they intermix with one another freely to form a homogeneous mixture. This process of intermixing of gas molecules is natural and spontaneous. This phenomenon is known as gaseous diffusion. *Diffusion means spreading out in all directions even against the gravity*. In general, diffusion is the passage of elementary particles through matter when there is high probability of scattering and less probability of capture.

Thus, *diffusion is defined as a phenomenon by which the gases intermix with one another to form a uniform mixture when they are brought in contact, due to the random movements of the gaseous molecules irrespective of their densities.*

In other words, *gaseous diffusion is the spontaneous intermixing of two or more gases of wide differences in their densities.* Diffusion also includes the passage of a gas through any porous wall e.g., porcelein, plaster of paris etc.

Experiment to illustrate the gaseous diffusion :

A jar filled with colourless and extremely light gas hydrogen is inverted over another jar filled with nitrogen dioxide which is reddish brown and much heavier than H_2. Within a few minutes, the appearance of light brown colour in the upper gas jar is observed. The colour in the upper jar progressively deepens while the colour in the lower jar slowly fades. After sometime the intensity of the colour in both the jars becomes identical. Chemical tests show that the gas in each gas jar is now found to be a mixture of H_2 and NO_2 of the same composition. NO_2 is much heavier than H_2, yet the heavier NO_2 molecules have moved upwards against the force of gravity, while the lighter molecules of hydrogen have moved downward disobeying the principle of gravity.

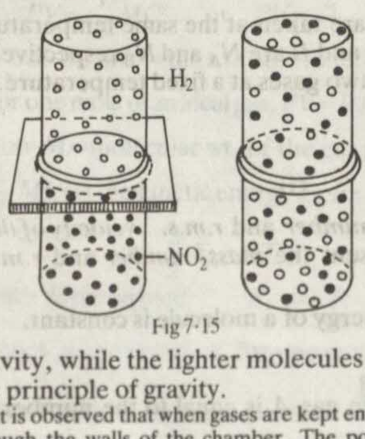


Fig 7·15

It is observed that when gases are kept enclosed in air tight chamber, their molecules slowly come out through the walls of the chamber. The porosity of all substances however are not the same, e.g., hydrogen gas comes out quickly when kept enclosed in a rubber baloon, but does not come out at all when enclosed in an iron vessel. The passage of gases through the walls of vessels is due to diffusion. Vessels made of plaster of Paris, clay, porcelain etc., are porous and the diffusion of gases takes place when the gases are kept in such containers.

- **Graham's law of diffusion :**

In 1846 the British scientist **Thomas Graham** was successful in establishing a quantitative relation between the *rate of diffusion* and the *relative density of a gas.*

He expressed this relation in the form of a law which is known as Graham's law of diffusion. The law states—

- *Under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their densities.*

Rate or velocity of diffusion of gases : *The rate or velocity of diffusion of a gas at constant temperature and pressure is defined as the volume of the gas in ml diffusing per unit time.* The rate of diffusion increases with the increase of temperature and pressure.

Let V ml of a gas diffuse out in t seconds

$\therefore$ The rate of diffusions of the gas $= \frac{V}{t}$ ml/sec.

or, Rate of diffusion of a gas $(r) = \dfrac{\text{Vol. of the gas diffused in ml}}{\text{Time taken in seconds}}$

If H_2 and CO_2 are kept in two different vessels of same porosity at the same temperature and pressure, H_2 will diffuse out of the vessel more quickly than CO_2. Since the relative density of CO_2 is much higher than that of H_2, the rate of diffusion of CO_2 is less than that of H_2.

• Mathematical expression of Graham's law—relation between the rate of diffusion and the density of gases :

Let at constant temperature and pressure the rate of diffusion of a gas be r and its density is D.

According to Graham's law, $r \propto \frac{1}{\sqrt{D}}$ · or, $r = \frac{K}{\sqrt{D}}$ K constant. Graham's law holds good when the densities of gases are expressed as normal densities or as relative densities.

Let r_1 and r_2 be the rate of diffusion of two different gases A and B having densities D_1 and D_2 respectively, at constant temperature and pressure. Then according to Graham's law,

$r_1 \propto K/\sqrt{D_1}$ and $r_2 = K/\sqrt{D_2}$

or, $r_1/r_2 = \sqrt{D_2}/\sqrt{D_1}$ i.e., $\dfrac{\text{rate of diffusion of } A}{\text{rate of diffusion of } B} = \dfrac{\sqrt{\text{density of } B}}{\sqrt{\text{density of } A}}$

$$= \frac{\sqrt{\text{relative density of } B}}{\sqrt{\text{relative density of } A}}$$

Thus by comparing the rates of diffusion of two gases at constant temperature and pressure it is possible to find out the vapour density of one if that of the other is known.

• Relation between the rate of diffusion and molecular weight of gases :

From Avogadro's law we know that—

Molecular weight of a gas = 2 × the vapour density

Let M_1 and M_2 be the molecular weights of two gases A and B respectively.

Then $D_1 = M_1/2$ and $D_2 = M_2/2$.

Since, $\frac{r_1}{r_2} = \sqrt{\frac{D_2}{D_1}}$ $\therefore$ $\frac{r_1}{r_2} = \sqrt{\frac{M_2/2}{M_1/2}}$ or, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

or, $\dfrac{\text{Rate of diffusion of } A}{\text{Rate of diffusion of } B} = \sqrt{\dfrac{\text{Molecular weight of } B}{\text{Molecular weight of } A}}$

or, $r \propto \frac{1}{M}$ for any gas.

Thus, *at constant temperature and pressure the ràte of diffusion of any gas is inversely proportional to the square root of its molecular weight.*

The Molecular weights of hydrogen and oxygen are 2 and 32 respectively.

$\therefore$ At constant temperature and pressure,

$$\frac{\text{Rate of diffusion of Hydrogen}}{\text{Rate of diffusion of Oxygen}} = \sqrt{\frac{32}{2}} = \frac{4}{1}$$

Thus, the rate of diffusion of hydrogen is four times that of oxygen gas at constant temperature and pressure, i.e., by the time when 1 volume of oxygen diffuses through a porous partition, 4 volumes of hydrogen will diffuse out. For the same reason, the rate of diffusion of CO_2 (Mol. wt. = 44) is much higher than that of SO_2 (Mol. wt. = 64) at constant temperature and pressure.

• Relation among the rate of diffusion, time of diffusion and relative density of a gas :

At constant temperature and pressure, *the rate of diffusion of any gas is inversely proportional its time of diffusion.*

or, $t \propto \frac{1}{r}$, t = time of diffusion, r = rate of diffusion.

If t_1 and t_2 be the times of diffusion of two gases at constant temperature and pressure and r_1 and r_2 be their rates of diffusion then—

$$t_1 \propto \frac{1}{r_1} \quad \text{and} \quad t_2 \propto \frac{1}{r_2} \qquad \text{or,} \quad \frac{t_1}{t_2} = \frac{r_2}{r_1}$$

$$\text{Again } \frac{r_2}{r_1} = \sqrt{\frac{D_1}{D_2}}$$

$$\therefore \frac{t_1}{t_2} = \frac{r_2}{r_1} = \sqrt{\frac{D_1}{D_2}} = \sqrt{\frac{M_1}{M_2}}$$

Hence *under the same conditions of temperature and pressure times required for equal volumes of two gases diffusing through a porous membrane are directly proportional to the square root of their relative densities or molecular weights.*

Since $\frac{r_H}{r_O} = 4$, it can be argued that when 100 ml of H_2 gas are diffused per second through a porous membrane only 25 ml of O_2 gas will be diffused out in one second.

• Relation between volume of gas diffused and its density.

We know $r = \frac{V}{t} = \frac{\text{Volume of gas in ml that diffuses}}{\text{Time of diffusion in seconds}}$

Let V_1 and V_2 be the volumes of two gases diffused in time t_1 and t_2 respectively under identical conditions of temperature and pressure.

$$\therefore \frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \frac{V_1}{t_1} \times \frac{t_2}{V_2}$$

$$\text{or, } \frac{r_1}{r_2} = \frac{V_1 t_2}{V_2 t_1} = \sqrt{\frac{D_2}{D_1}} = \sqrt{\frac{M_2}{M_1}}$$

If times of diffusion of two gases are same i.e., $t_1 = t_2$

$$\therefore \frac{r_1}{r_2} = \frac{V_1}{V_2} \quad \sqrt{\frac{D_2}{D_1}} = \sqrt{\frac{M_2}{M_1}}$$

Or, in other words, *under the identical conditions of temperature and pressure the volumes of two gases diffusing through porous membrane in any given time is inversely proportional to the square root of their relative densities or molecular weights.*

• Validity of Graham's Law :

When reciprocal of the rates of diffusion are plotted against the square roots of the densities of gases, a straight line is obtained. This graph indicates that the rate of diffusion of a gas is inversely proportional to the square root of its density (Fig 7·16).

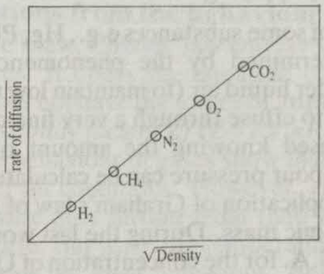


Fig 7·16 : Graphical representation of Graham's Law's experimental data

7·12. Effusion of gas.

Diffusion is in fact intermolecular mixing of substances *without the application of pressure* since the propagation of the molecules is a spontaneous one. Complete miscibility of gases is attributed to gaseous diffusion. However, if gases are allowed to *pass under pressure* from an enclosed vessel through a fine orifice into the air outside, the gas will diffuse into air but air will not enter into the gas inside. This phenomenon is termed as *Effusion.*

Hence, *effusion is the process of allowing a gas confined in a closed container under pressure to escape through a fine orifice made in the wall of the container.*

Thus while diffusion is a spontaneous mixing up of gas molecules irrespective of density and pressure, effusion is the escape of gas through a fine orifice under pressure. Effusion is a special case of diffusion where the gas is allowed to escape through a fine orifice.

Graham's Law is also applicable to effusion i.e., *the rates of effusion of gases through a small aperture under the identical conditions of temperature and pressure are inversely proportional to the square roots of their relative densities or molecular weights.* Measurements of the rate of diffusion is very difficult. Hence it is determined by measuring the rate of effusion which consists in passing equal volumes of two gases through the same orifice under the same conditions of temperature and pressure.

• Practical applications of diffusion :

1. The most important practical application of gaseous diffusion is the detection of Marsh gas (Methane) in coal mines. Marsh gas forms an explosively inflammable mixture with air and thus causes explosion inside the mines. The Marsh gas detector consists of a porous pot which is connected with one limb of a glass U-tube by means of a glass tube and a rubber cork. The U-tube is filled with mercury. Two platinum wires are fitted with two limbs of the U-tube—one is connected with the mercury in one limb and the other is just above the mercury level in the other limb. The two wires are connected with the battary through an electric bell. A big glass jar is kept inverted over the porous pot. Methane is lighter than air and so it diffuses more quickly into the porous pot and pushes the mercury level. As a result the mercury level comes in contact with the platinum wire of the other limb and thus electric circuit being completed the bell rings.

2. Separation of individual gases of different densities and rates of diffusion from their mixture is another practical application of diffusion. The process is called *Atomolysis*.

3. The differences in the rates of diffusion of gases enable us to determine the *molecular weights* of gases by applying the Graham's law of diffusion.

4. The vapour pressure of some substances e.g., Hg, Pb etc. which volatilise with difficulty can also be determined by the phenomenon of effusion. A highly evacuated vessel is kept under liquid air (to maintain low temperature). The vapour of the substance is allowed to effuse through a very fine orifice into the vessel. The vapour is at once condensed knowing the amount of substance escaped and dimension of orifice, the vapour pressure can be calculated.

5. Another important application of Graham's law of diffusion is the separation of Isotopes of different atomic mass. During the last world war, a very large plant was built at Oak Ridge, U.S.A. for the concentration of U^{235}. U^{235} occurs in natural uranium to the extent of only 0·72 percent. Volatile UF_6 was chosen partly because fluorine exists in nature as a single isotope. The molecular masses of $U^{238}F_6$ and $U^{235}F_6$ are different and the ratio of the square roots of their molecular masses is only 1·0043. Hence a large number of diffusions are required. The molecules containing $U^{235}F_6$ diffuse out faster than the molecules containing $U^{238}F_6$ under a difference of pressure. In order to ensure a ready flow through the porous barrier, the diameter of the pores should be less than 1/10 th of the mean free path of the gas molecules. Separation process was massive and about 4000 diffusion stages were required to increase the concentration of U^{235} abundance from 0·72 percent to 99 percent.

• Experimental Verification of Law of Diffusion :

It can be demonstrated experimentally that gases with lower density diffuse out faster than gases with higher density. A porous cell like that used in batteries is fitted with a rubber cork through which a long glass tube is introduced. The tube contains a bulb and a fine jet at the outer end and bent in the form of a U-tube. The whole arrangement is set up in vertical position as shown in Fig. 7·17.

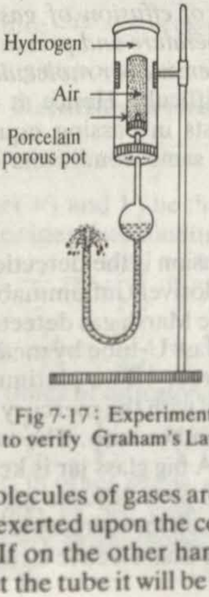


Fig 7·17 : Experiment to verify Graham's Law

The tube is next detached from the porcelain porous cell and the lower part of the tube is filled with some coloured water. The U-tube is next attached to the porcelain cell through the rubber cork. The porcelain cell is next covered with a gas jar filled with hydrogen gas. It will be observed that coloured water is forced out of the jet in the form of a fountain.

Explanation : The porcelain porous cell contains air. As soon as the cell is covered with hydrogen containing gas jar, hydrogen being much lighter than air, rushes more quickly through the pores of the walls into the cell, than the air inside the cell which comes out. As a result the number of molecules of gases are increased inside the cell, with the result that greater pressure is exerted upon the coloured water, which is forced out in the form of a fountain.

If on the other hand hydrogen is replaced by CO_2 then instead of water coming out the tube it will be observed that water is rising upward from the bulb towards the porcelain cell. This is because density of CO_2 being higher than the air, CO_2 cannot diffuse inside the cell, instead air will effuse through the pores of the cell into CO_2 atmosphere. As a result the pressure inside the cell will decrease and coloured water will slowly rise up.

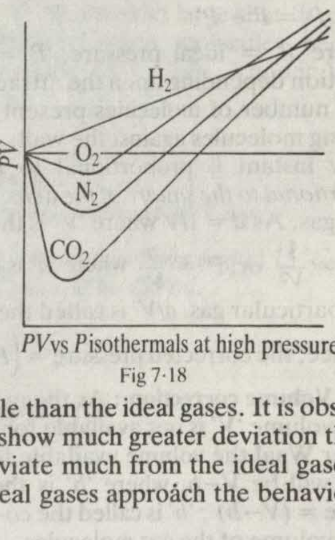
- **Real gases—deviations from the behaviour of ideal gas :**

An ideal gas obeys Boyle's law, Charles' law and Avogadro's law for all values of temperatures and pressures. It obeys the equation of state $PV=nRT$ under all conditions. An ideal gas does not have the forces of attraction or repulsion between its molecules. The *compressibility factor (Z)* $(Z=PV/nRT)$ of an ideal gas = 1.

Extensive studies on the behaviour of gases show that no gas obeys the ideal gas equation $PV = nRT$ under all conditions. However, all gases approach the ideal behaviour as the temperature goes further from their boilling points i.e., at high temperature and low pressure. But when the temperature is low and the pressure is high, the gases deviate from the ideal behaviour. Boyle's experiments were all performed at ordinary temperatures and pressures and his law was based on the results of these experiments. But when the experiments were performed at high pressures and low temperatures it was found that the law was applicable only as an approximation.

For a fixed quantity of an ideal gas at constant temperature PV should remain constant inspite of the variation of P and consequently a plot PV against P will be a straight line parallel to the X-axis It has been observed that in case of real gases the plots of PV against P are linear but not parallel to the X-axis. At high pressure, the plots of PV first decrease and then after reaching a minimum, rise with the increase of pressure. In case of H_2 and He, the value PV increases steadily with the increase of pressure from the very beginning.

From these curves it is clearly found that at low pressure the gases are more compressible than the ideal gases and at high pressures the gases are less compressible than the ideal gases. It is observed that at low temperature the curves in general show much greater deviation than at high temperature. Easily liquefiable gases deviate much from the ideal gases. At very low pressure and high temperature the real gases approach the behaviour of ideal gas.



PV vs *P* isothermals at high pressure

Fig 7·18

- **Causes for the deviation of real gases from ideal behaviour :**

According to Vander Waal the real gases deviate from the ideal behaviour as the following assumptions of kinetic theory of gases are not applicable for them.

(i) The gas molecules are perfectly elastic and there being no intermolecular forces of attraction or repulsion between the molecules, they are in a continuous random movement in all possible directions.

(ii) The volume occupied by the gaseous molecules is negligibly small as compared to the total volume occupied by the gas.

These two assumptions do not hold good for real gases at high pressure and low temperature. The liquefaction of gases by the application of pressure below critical

temperature and that all real gases exhibit Joule-Thomson cooling below their inversion temperatures, clearly proves the existense of inter molucular forces of attraction between the gas molecules at low temperatures.

- **Vander Waal's equation :**

(a) **Pressure correction :** The intermolecular forces of attraction between the molecules do play when the gaseous molecules come closer to one another by the application of high pressure on the gas. A gaseous molecule which is present in the interior part of the vessel is sorrounded by the other molecules on all sides. It is thus attracted by the other molecules equally from all directions. As a result, this molecule does not experience any resultant attractive force. Now a molecule which is about to strike the wall of the vessel, will experience an inward pull from the large number of molecules present in the interior part of the gas. As a result some part of its outward motion is used up in overcoming the inward attractive forces. Consequently this molecule will not collide against the wall of the vessel with the same force if it were not being pulled back by the inward attractive forces. As a result, the observed pressure will be less than the ideal pressure, i.e., the ideal pressure is equal to the observed pressure plus a pressure correction.

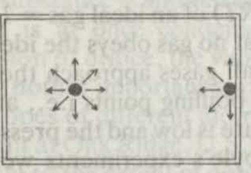


Fig 7·19

or, $P_i = P + P'$

where P_i = ideal pressure, P = observed pressure and P' = the pressure correction depending upon the attractive force. The attractive force is proportional to the number of molecules present in the interior part of the gas which pull the colliding molecules against the wall. Again since the number of colliding molecules at any instant is proportional to the number present, the attractive force is *proportional to the square of the density of the gas* i.e., $P' \propto d^2$ where 'd' is the density of the gas. As $d = 1/V$ where 'V' is the volume of the gas,

$\therefore\ P' \propto \frac{1}{V^2}$ or, $P' = \frac{a}{V^2}$ where 'a' is the attraction per unit volume which is constant for a particular gas. a/V^2 is called the *internal pressure* or *cohesive pressure*.

Hence, the corrected pressure $= \left(P + \frac{a}{V^2}\right)$

(b) **Volume correction :** As the molecules of a real gas occupy some volume, the entire volume 'V' is not available for the movement of the molecules. According to Vander Waal the volume available for the free movements of the molecules in the vessel will be $V-b$, where 'b' is the nonavailable volume ; hence the corrected volume = $(V-b)$; 'b' is called the *co-volume*. It is found that 'b' is nearly 4 times the actual volume of the gas molecules.

Thus, by applying these two corrections in the gas equation $PV = RT$ we get,

$\left(P + \frac{a}{V^2}\right)(V - b) = RT$. for *one mole of the gas.*

This equation is known as Vander Waal's equation.

If in the volume V of the gas, the number of moles present be 'n', the volume of one mole of the gas would be V/n.

Hence, $\left[P + \frac{a}{(V/n)^2}\right](V/n - b) = RT$

or, $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ **(for n moles of a gas)**

- **Application of Vander Waal's equation :**

Vander Waal's equation can explain the behaviour of real gases under different conditions. It holds good for real gases even at *high temperature*. From Vander Waal's equation we get,

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

$$\text{or, } PV-Pb+a/V-ab/V^2=RT$$

$$\text{or, } PV=RT+Pb-a/V+ab/V^2 \cdots\ \cdots\ \cdots (1)$$

(i) *At low pressure* P is small and V is much greater, consequently factors Pb and ab/V^2 become too small and so these two factors can be neglected. Hence the equation takes the form $PV = RT - a/V$.

In this equation, we see that $PV < RT$. Now with the increase of pressure 'V' decreases and the value of a/V increases. Consequently at low pressure the value of PV decreases with the increase of P. This is what we find in case of real gases.

(ii) *At high pressure* as V becomes small, the factor Pb over weights the factor a/V. In this case the equation (1) can be written as, $PV = RT + Pb$.

i.e., $PV>RT$. With the increase of 'P' the value of PV goes on increasing. This is what is observed by the ascending part of PV vs P curve after reaching the minimum.

(iii) *At low temperature,* both P and V are small and hence the volume and pressure corrections should be taken into account. Consequently, real gases deviate much from the ideal behaviour.

(iv) *At high temperature and low pressure,* 'V' becomes so large that 'b' can be neglected. Under this condition the attraction between molecules becomes negligible and so the factor a/V^2 can be neglected. As a result, Vander Waal's equation reduces to $PV = RT$.

7.13. Numerical problems on gas laws.

[A] Calculations involving Boyle's Law and Charles' Law :

1. *The volume of a certain mass of a gas at a constant pressure and at 15 °C is 360 ml. Find the temperature of the gas when its volume will be 480 ml.*

Ans : From Charles' Law,

$$\frac{V_1}{T_1}=\frac{V_2}{T_2} \quad \text{(at constant pressure)}$$

Here, $V_1 = 360$ ml, $T_1 = 273 + 15 = 288$K, $V_2 = 480$ ml, $T_2 = ?$

Putting the values of V_1, T_1 and V_2

$$\text{or, } \frac{360}{288}=\frac{480}{T_2}$$

$$\text{or, } T_2=\frac{480\times 288}{360}=384\text{K}$$

$$\text{or, } T_2=384-273=111^\circ\text{C}$$

2. *The volume of a given mass of a gas is 2000 ml at 27°C and 760 mm pressure. Calculate the volume of the gas at 327°C and 1520 mm pressure.*

Ans : We know $\dfrac{P_1V_1}{T_1}=\dfrac{P_2V_2}{T_2}$

Here, $P_1 = 760$ mm　　$P_2 = 1520$ mm
$V_1 = 2000$ ml　　$V_2 = ?$
$T_1 = 273 + 27 = 300$K　　$T_2 = 273 + 327 = 600$K

$$\text{or, } \frac{760\times 2000}{300}=\frac{1520\times V_2}{600}$$

or, $V_2 = \dfrac{760 \times 2000 \times 600}{300 \times 1520} = 2000$ ml.

3. *The volume of 1 gram mole of oxygen gas is 22400 ml at 760 mm. Calculate the temperature of the gas (Given R = 0·082 lit-atmos deg^{-1} mole^{-1}).*

Ans : For 1 mole of an ideal gas

$$PV = RT$$

or $T = \dfrac{PV}{R}$ $\qquad P = 760$ mm $= 1$ atmos

$V = 22400$ ml $= 22{\cdot}4$ litre

$$T = \frac{1 \times 22{\cdot}4}{0{\cdot}082} = 273{\cdot}17\text{K}$$

or, temperature in celsius scale

$= (273{\cdot}17 - 273) = 0{\cdot}17$°C

4. *A gas cylinder contains hydrogen gas at 27°C and 20 atmosphere pressure. The cylinder holds 2·82 litres of water. Calculate the number of spherical balloons of diameter 21 cm which will be filled up by hydrogen gas at N.T.P.* [I.I.T. 1987]

Ans : The volume of the balloon $= \dfrac{4}{3}\pi r^3 = \dfrac{4}{3} \times \dfrac{22}{7} \times \left(\dfrac{21}{2}\right)^3$

$= 4851$ ml

Let V be the volume of hydrogen in the cylinder at N.T.P.

$$\frac{1 \times V}{273} = \frac{20 \times 2820}{300} \quad \text{or,} \quad V = \frac{273 \times 20 \times 2820}{300} = 51324 \text{ ml}$$

Out of this volume, 2820 ml of hydrogen will be present in the cylinder, hence the volume of hydrogen required for filling the balloon = 51324 − 2820 = 48504 ml.

$\therefore$ Number of balloons $= \dfrac{48504}{4851} \approx 10$

5. *A gas cylinder can withstand a pressure upto 300 atmospheres. Now a certain quantity of gas is introduced into the cylinder at 27°C and 150 atmospheres pressure and is heated. At what temperature will the cylinder explode ?*

Ans : Let the volume of the cylinder be V ml

Initially :	Finally when it bursts
V_1 volume $= V$	V_2 volume $= V$
P_1 pressure = 150 atmosphere	P_2 pressure = 300 atmosphere
T_1 temperature = 273 + 27 = 300K	$T_2 = ?$

Applying the formula,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{or,} \quad \frac{150 \times V}{300} = \frac{300 \times V}{T_2}$$

or, $T_2 = \dfrac{300 \times 300}{150} = 600$K

Temperature in celsius scale = (600 − 273) = 327°C

6. *If the density of a given mass of gas at 27°C and 760 mm pressure is 22, what will be its density at 127°C and 1140 mm pressure ?*

Ans : Here initial pressure $(P_1) =$ 760 mm

,, density $(D_1) =$ 22

,, temperature $(T_1) =$ 273 + 27 = 300K

Final Pressure $(P_2) =$ 1140 mm

,, temperature $(T_2) =$ 273 + 127 = 400 K

,, density $(D_2) = ?$

Let the initial volume be V_1 ml and final volume V_2 ml and mass of gas = m g.

$$\therefore V_1 = \frac{m}{D_1},\ V_2 = \frac{m}{D_2}$$

Since $P_1V_1 = RT_1$ or, $P_1\dfrac{m}{D_1} = RT_1$ or, $P_1 = \dfrac{D_1RT_1}{m}$

Similarly $P_2 = \dfrac{D_2RT_2}{m}$

or, $\dfrac{P_1}{P_2} = \dfrac{D_1T_1}{D_2T_2}$ or, $D_2 = \dfrac{D_1T_1P_2}{P_1T_2}$

$$= \frac{22 \times 300 \times 1140}{400 \times 760} = 24{\cdot}75$$

8. *Assume the centre of the sun to consist of gases whose average molecular weight is 2·0. The density and pressure of the gases are 1·3 g/cc and 1·12×10⁹ atmosphere respectively. Calculate the temperature of the sun.* *(I.I.T. 1966)*

Ans : We know for *n* moles of an ideal gas $PV = nRT$

For 1 mole of ideal gas, $n = 1$

or, $PV = RT$

$\therefore \quad T = \dfrac{PV}{R}$

Volume occupied by 2 g of the gas $= \dfrac{2}{1{\cdot}3 \times 1000}$ litre.

$$T = \frac{1{\cdot}12 \times 10^9 \times 2}{0{\cdot}082 \times 1{\cdot}3 \times 1000} = 2{\cdot}101 \times 10^7\text{K}$$

9. *When 3·2 g of sulphur is heated it occupies a volume of 780 ml at 450°C and 723 mm pressure. Calculate the formula of sulphur at that condition.* *(I.I.T. 1968)*

Ans : Let the volume of sulphur vapour at N.T.P. be V_1.

$P_1 = 760$ mm $\quad T_1 = 273$K

$P_2 = 723$ mm $\quad V_2 = 780$ ml $\quad T_2 = 450 + 273 = 723$K

$\dfrac{V_1 \times 760}{273} = \dfrac{780 \times 723}{723}$ or, $V_1 = \dfrac{780 \times 273}{760}$ ml

Weight of $\dfrac{780 \times 273}{760}$ ml of sulphur vapour at N.T.P. is 3·2 g

Weight of 22400 ml of Sulphur vapour at N.T.P. is $\dfrac{3{\cdot}2 \times 22400 \times 760}{780 \times 273} = 225{\cdot}83$ g.

$\therefore$ Molecular weight of sulphur = 225·83

Since the atomic weight of sulphur = 32

$\therefore$ Atomicity of sulphur $= \dfrac{225{\cdot}83}{32} = 7{\cdot}995 \simeq 8$

$\therefore$ Molecular formula of sulphur = S_8

10. *A gas cylinder containing cooking gas can withstand a pressure of 14·9 atmosphere. The pressure gauge of the cylinder indicates 12 atmosphere at 27°C. Due to a sudden fire in the building, the temperature starts rising. At what temperature will the cylinder explode ?* *[I.I.T. 1975]*

Ans : The cylinder will explode as soon as the pressure exceeds 14·9 atmosphere.

$P_1 = 12$ atmosphere $\quad T_1 = 273 + 27 = 300$K

$P_2 = 14{\cdot}9$ atmosphere $\quad T_2 = ?$

Now $\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$

or, $\dfrac{12}{300} = \dfrac{14{\cdot}9}{T_2}$ or, $T_2 = 372{\cdot}5$K

$\therefore$ The temperature when the cylinder will explode $= 372{\cdot}5 - 273 = 99{\cdot}5$°C.

11. *An open vessel at 27°C is heated until three fifth of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated.* [*I.I.T. 1977*]

Ans : Here the volume is constant, as the vessel is open, the pressure is also constant. Let at the initial state n_1 moles are present in the vessel and in the final state n_2 *moles are present in the vessel. Let* T_1 *and* T_2 *are the initial and final temperatures of the gas respectively. So the gas eq. for the two cases becomes* $PV = n_1RT_1$ *and* $PV = n_2RT_2$

or, $n_1RT_1 = n_2RT_2$ *or,* $n_1T_1 = n_2T_2$...... *(i)*

Let in the initial state the number of moles = 1

As the number of moles is proportional to the volume of the gas, the final number of moles $n_2 = 1 - 3/5 = 0{\cdot}4$ $T_1 = 27 + 273 = 300\text{K}, T_2 = ?$

Substituting the values in (i)

$$1 \times 300 = 0{\cdot}4 \times T_2 \quad \text{or, } T_2 = 750\,\text{K}$$

$\therefore$ Temp. in celsious = 750 − 273 = 477°C.

12. *When 2·0 g of a gas A is introduced into an evacuated flask kept at 25°C, the pressure is found to be 1 atmosphere. If 3·0 g of another gas B is then added to the same flask, the total pressure becomes 0·5 atmosphere. Assuming ideal gas behaviour calculate the ratio of molecular weights* $M_A : A_B$. [*I.I.T. 1983*]

Ans : Applying Ideal gas equation for *n* moles

$$PV = nRT$$

$$PV = \frac{g}{M}RT$$

$$M = \frac{gRT}{PV}$$

Let the molecular weights of two gases be M_A and M_B

$$\therefore M_A = 2 \times \frac{RT}{1 \times V} \quad \text{and } M_B = \frac{3 \times RT}{0{\cdot}5 \times V}$$

$$\text{or, } \frac{M_A}{M_B} = \frac{2RT}{V} \times \frac{0{\cdot}5V}{3RT} = \frac{2 \times 0{\cdot}5}{3} = \frac{1}{3}$$

or, the ratio $M_A : M_B = 1 : 3$

[B] Problems on partial pressure :

13. *A mixture of gases at 760 mm pressure contains 80% nitrogen and 20% oxygen. What is the partial pressure of the gas ?* [*W.B.J.E.E. 1985*]

Ans : Let P_N = Partial pressure of nitrogen

P_O = ,, ,, ,, oxygen

Total pressure $(P) = P_N + P_O = 760$ mm

$$\therefore P_N = \frac{760 \times 80}{100} = 608\,\text{mm}$$

$$P_O = \frac{760 \times 20}{100} = 152\,\text{mm}$$

14. *300 ml of nitrogen and 200 ml of* CO_2 *gas are taken in a 500 ml flask. The pressure of nitrogen and* CO_2 *are 200 mm and 400 mm respectively. Find the total pressure of the gas mixture.*

Ans : The volume of the vessel (V_1) = 500 ml

Let P_N and P_{CO_2} be the partial pressures of Nitrogen and CO_2 respectively.

The pressure of Nitrogen (P_1) = 200 mm ; Pressure of CO_2 (P_2) = 400 mm

" volume " " (V_1) = 300 ml ; Volume " " (V_2) = 200 mm

According Boyle's Law,

$$P_1V_1 = P_N(V_1 + V_2)$$

$$\text{or,} \quad P_N = \frac{P_1V_1}{V_1 + V_2} = \frac{200 \times 300}{300 + 200} = 120\,\text{mm}$$

$$\text{Again,} \quad P_2V_2 = P_{CO_2}(V_1 + V_2)$$

$$P_{CO_2} = \frac{P_2V_2}{V_1 + V_2} = \frac{400 \times 200}{300 + 200} = 160\,\text{mm}$$

$\therefore$ Total pressure $= P_N + P_{CO2}$

$= 120 + 160 = 280$ mm

15. *100 ml of O_2 and 75 ml of H_2 at N.T.P. are introduced into a glass vessel of capacity 400 ml at 0°C. Find the total pressure of the gas mixture and the partial pressure of O_2 and H_2.*

Ans : Volume of $O_2 = 100$ ml   Pressue $= 760$ mm
Volume of $H_2 = 75$ ml   Pressue $= 760$ mm

Volume of the gas mixture at N.T.P. $= 100 + 75 = 175$ ml

Since this gas mixture is taken into a vessel of capacity 400 ml hence the final volume $= 400$ ml

Let the final pressure be P

$$\therefore \quad \frac{P_1V_1}{T_1} = \frac{PV}{T}$$

Here $P_1 = 760$ mm $V_1 = 175$ ml $T_1 = 273$K
$P =$ unknown $V = 400$ ml $T = 273$K

$$\therefore \quad \frac{760 \times 175}{273} = \frac{P \times 400}{273} \quad \text{or,} \quad P = 332{\cdot}5\,\text{mm}$$

$\therefore$ Total pressure of the gas mixture $= 332{\cdot}5$ mm

Let the partial pressure of O_2 and H_2 be p_1 and p_2 respectively before introducing the gases into 400 ml glass vessel

$$p_1 = \frac{760 \times 100}{175}\ \text{mm}$$

$$p_2 = \frac{760 \times 75}{175}\ \text{mm}$$

On keeping the gases at the 400 ml glass vessel let their partial pressure become p_0 and p_H.

Since temperature 0°C is constant, applying Boyle's Law,

$$P_1V_1 = P_2V_2$$

$$p_1 \times 175 = P_0 \times 400$$

$$\text{or,} \quad \frac{760 \times 100}{175} \times 175 = P_0 \times 400$$

$$P_0 = \frac{760 \times 100}{400} = 190\,\text{mm.}$$

$$\text{Again,} \quad P_2 \times 175 = p_{H_2} \times 400$$

$$\text{or,} \quad \frac{760 \times 75}{175} \times 175 = p_{H_2} \times 400$$

$$p_{H_2} = \frac{760 \times 75}{400} = 142{\cdot}5\,\text{mm}$$

16. *A mixture of 2·0 g of hydrogen and 8·0 g of oxygen is kept in a vessel of 20 litre capacity at 27°C. What is the total pressure inside the vessel ?* [*W.B.H.S. 1982*]

Ans : $2\,\text{g of } H_2 = \frac{2}{2} = 1$ mole

$8\,\text{g of } O_2 = \frac{8}{32} = 0{\cdot}25$ mole

The volume of the gas mixture (V) $= 20$ litres

temperature $= 273 + 27 = 300$K

We know, $PV = nRT$

or, $P = \dfrac{nRT}{V}$

Partial pressure of H_2 $= \dfrac{1 \times 0{\cdot}082 \times 300}{20} = 1{\cdot}23$ atmos

" " " O_2 $= \dfrac{0{\cdot}25 \times 0{\cdot}082 \times 300}{20} = 0{\cdot}3075$ atmos

Hence total pressure = 1·23 + 0·3075 = 1·5375 atmosphere

17. *A gaseous mixture is prepared at 200 k Pa and 50°C by mixing 0·4 g of H_2, 4·2 g of N_2 and 3·2 g of O_2. Calculate (i) the number of moles, (ii) mole fraction and (iii) the partial pressure of each gas of the mixture.*

Ans : (a) mole $= \dfrac{\text{wt. of the gas}}{\text{mol. wt.}} = n = \dfrac{W}{M}$

∴ No. of moles of H_2 $= \dfrac{0{\cdot}4}{2} = 0{\cdot}2$ mole

No. of moles of N_2 $= \dfrac{4{\cdot}2}{28} = 0{\cdot}15$ mole

No. of moles of O_2 $= \dfrac{3{\cdot}2}{32} = 0{\cdot}1$ mole

∴ The total number of moles = 0·2 + 0·15 + 0·1 = 0·45 moles

(ii) Mole fraction of A = x^A = mole of A/total moles

∴ mole fraction of $H_2 = x_{H_2}$ = 0·2/0·45 = 0·444

∴ mole fraction of $N_2 = x_{N2}$ = 0·15/0·745 = 0·333

mole fraction of $O_2 = x_{O_2}$ = 0·1/0·45 = 0·222

(iii) According to Dalton's law of partial pressure,

Partial pressure P_A = mole fraction of A × Total pressure

∴ $P_{H_2} = 0{\cdot}444 \times 200$ k Pa $= 88{\cdot}8$ k Pa

$P_{N_2} = 0{\cdot}333 \times 200$ k Pa $= 66{\cdot}6$ k Pa

$P_{N_2} = 0{\cdot}222 \times 200$ k Pa $= 44{\cdot}4$ k Pa

18. *0·02 mole of CH_4 and 0·06 mole of O_2 are taken in a vessel at 27°C and 101325 Nm^{-2} and the mixture is ignited when reaction takes place according to the equation.*

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$$

Calculate (i) the volume of the flask, (ii) the total pressure and the partial pressures of CH_4 and O_2 before and after the reaction at 27°C.

Ans : We know that $PV = nRT$

∴ the volume of the flask $V = \dfrac{nRT}{P}$

data given $T = 27 + 273 = 300$ K, $P = 101325\ Nm^{-2}$

n = Total number of moles present before the reaction = 0·02 + 0·06 = 0·08 moles.

$$\therefore V = \frac{0{\cdot}08 \times 8{\cdot}314 \times 300}{101325}$$

$$= 1{\cdot}97 \times 10^{-3}\,m^3$$

Before reation :

Mole fraction of CH_4 = 0·02/0·08 = 0·25

Mole fraction of O_2 = 0·06/0·08 = 0·75

∴ Partial pressure of CH_4 = 0·25 × 101325 Nm^{-2} = 25331 Nm^{-2}

Partial pressure of O_2 = 0·75 × 101325 Nm^{-2} = 75994 Nm^{-2}

After the reaction :

$$\begin{array}{ccccccc} CH_4(g) & + & 2O_2(g) & \rightarrow & CO(g) & + & 2H_2O(g) \\ \text{1 mole} & & \text{2 moles} & & \text{1 mole} & & \text{2 moles} \\ \text{0·02 mole} & & \text{0·04 mole} & & \text{0·02 mole} & & \text{0·04 mole} \end{array}$$

Thus after the completion of the reaction CH_4 would not be left as residue. 0·02 moles of CH_4 reacts with 0·04 moles of O_2. Therefore $0{\cdot}06 - 0{\cdot}04 = 0{\cdot}02$ moles of O_2 will be left unreacted. As product 0·02 mole of CO_2 and 0·04 mole of steam will be produced.

thus the total moles $= 0{\cdot}02 + 0{\cdot}02 + 0{\cdot}04 = 0{\cdot}08$ mole
mole fraction of O_2 $= 0{\cdot}02/0{\cdot}08 = 0{\cdot}25$
" " " CO_2 $= 0{\cdot}02/0{\cdot}08 = 0{\cdot}25$
" " " H_2O $= 0{\cdot}04/0{\cdot}08 = 0{\cdot}5$
$\therefore$ Partial pressure of O_2 $= 0{\cdot}25 \times 101325\ \text{Nm}^{-2} = 25331{\cdot}25\ \text{Nm}^{-2}$
" " " CO_2 $= 0{\cdot}25 \times 101325\ \text{Nm}^{-2} = 25331{\cdot}25\ \text{Nm}^{-2}$
" " " H_2O $= 0{\cdot}50 \times 101325\ \text{Nm}^{-2} = 50662{\cdot}5\ \text{Nm}^{-2}$

[C] On Kinetic theory of gases :

19. *Calculate the kinetic energy of 10 moles of an ideal gas at 0°C.*

Ans : We know that $E_K = 3/2\ RT$ for 1 mole of an ideal gas.

$\therefore$ For 10 moles, $E_K = 10 \times 3/2\ RT$

Now $R = 8{\cdot}314\ \text{Nm K}^{-1}\text{mol}^{-1}$; $T = 273 + 0 = 273\text{K}$

$\therefore E_K = 10 \times (3/2) \times 8{\cdot}314\ \text{Nm mol}^{-1}\text{K}^{-1} \times 273\text{K}$

$= 34045{\cdot}8$ joules.

20. *Determine the kinetic energy of 5 g of ammonia of 27°C.*

Ans : 5 g of $NH_3 = 5/17 = 0{\cdot}294$ moles

$T = 273 + 27 = 300$ K.

$\therefore E_K = 3/2\ RT = 0{\cdot}0294 \times (3/2) \times 8{\cdot}314\ \text{JK}^{-1}\text{mole}^{-1} \times 300\ \text{K}$

$= 1099{\cdot}94$ joules.

21. *What is the root mean square velocity of oxygen at 300 K ?*

Ans : We know $C^2 = 3RT/M$

Here, $T = 300\ \text{K}$, $M = \dfrac{32}{1000} = 0{\cdot}032\ \text{kg mol}^{-1}$

$R = 8{\cdot}314\ \text{J K}^{-1}\text{mol}^{-1} = 8{\cdot}314\ \text{Nm mol}^{-1}\text{K}^{-1} = 8{\cdot}314\ \text{kg m}^2\text{Sec}^{-2}\text{mol}^{-1}\text{K}^{-1}$

$$\therefore C^2 = \frac{3 \times 8{\cdot}314\ \text{kg m}^2\text{sec}^{-2}\text{mol}^{-1}\text{K}^{-1} \times 300\ \text{K}}{0{\cdot}032\ \text{kg mol}^{-1}}$$

$= 233831\ \text{m}^2\text{s}^{-2}$

$C = \sqrt{233831\ \text{m}^2\text{sec}^{-2}} = 483{\cdot}5\ \text{m s}^{-1}$

22. *Find the root mean square velocity of H_2 molecules at N.T.P.*

Ans : Here, $P = 101300$ Pa (Standard pressure in S.I. unit)

$V = 22{\cdot}4\ \text{L mol}^{-1} = 22{\cdot}4 \times 10^{-3}\ \text{m}^3\text{mol}^{-1}$

$M = 2\ \text{g mol}^{-1} = 2 \times 10^{-3}\text{kg mol}^{-1}$

$$C^2 = \frac{3PV}{M} = \frac{3 \times 101300 \times 22{\cdot}4 \times 10^{-3}}{2 \times 10^{-3}} = 3403680$$

$\therefore C = \sqrt{3403680} = 1845\ \text{m s}^{-1}$

23. *Calculate the average Kinetic energy in joules, of molecules in 8·0 g of methane at 300 K.* *[I.I.T. '82]*

Ans : We know, Total K.E. $= 3/2\ nRT$

Where, n = number of moles of the gas $= 8/16 = 0{\cdot}5$ mole

$R = 8{\cdot}314$ Joules $\text{K}^{-1}\text{mole}^{-1}$

$T = 300$ K.

$\therefore$ The K.E. $= 3/2 \times 0{\cdot}5 \times 8{\cdot}314 \times 300$

$= 1870{\cdot}65$ Joules

$$\therefore \text{Average K.E.} = \frac{1870{\cdot}65}{6{\cdot}023 \times 10^{23} \times 0{\cdot}5} = 6{\cdot}21 \times 10^{-21}\ \text{Joules}$$

24. *Calculate the pressure exerted by 0·5 mole CO_2 contained in a 0·5 litre vessel at 298K by using Vander Waal's equation when (i) $a = 0$ but $b = 0{\cdot}04267\ L\ mole^{-1}$, (ii) $a = 3{\cdot}592\ atmos\ L^2\ mole^{-2}$ but $b = 0$, (iii) $a = b = 0$.*

Ans : From Vander Waal's equation we get,

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

(i) Here, $a = 0$ and $b = 0{\cdot}04267\ \text{L mole}^{-1}$

$$\therefore\ P = \frac{0{\cdot}5\ \text{mol} \times 0{\cdot}082\ \text{L atmos K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{0{\cdot}5\ \text{L} - 0{\cdot}5\ \text{mol} \times 0{\cdot}04267\ \text{L mol}^{-1}} - \frac{0 \times (0{\cdot}5\ \text{mol})^2}{(0{\cdot}5\ \text{L})^2}$$

or, $P = 25{\cdot}5$ atmos.

(ii) Here, $a = 3{\cdot}592\ \text{atmos L}^2\ \text{mole}^{-2}$ and $b = 0$

$$\therefore\ P = \frac{0{\cdot}5\ \text{mol} \times 0{\cdot}082\ \text{L atmos K}^{-1}\ \text{mol}^{-1} \times 298\text{K}}{0{\cdot}5\ \text{L}} - \frac{(3{\cdot}592\ \text{atmos L}^2\ \text{mol})^{-2} \times (0{\cdot}5)^2}{(0{\cdot}5\ \text{L})^2}$$

$$= 24{\cdot}4\ \text{atmos} - 3{\cdot}592\ \text{atmos} = 20{\cdot}8\ \text{atmos}$$

(iii) Here $a = 0$ and $b = 0$

$$\therefore\ P = \frac{0{\cdot}5\ \text{mol} \times 0{\cdot}082\ \text{atms L K}^{-1}\ \text{mol}^{-1} \times 298\text{K}}{0{\cdot}5\ \text{L}} = 24{\cdot}4\ \text{atmosphere.}$$

[D] Problems on Diffusion of gases :

25. *16 ml of hydrogen is diffused in 30 seconds. Find the volume of SO_2 gas which will be diffused at the same time.*

Ans : Let x ml of SO_2 be diffused in 30 sec

The rate of diffusion of $H_2 = \frac{16}{30}$ ml/sec

$\therefore$ The rate of diffusion of $SO_2 = \frac{x}{30}$ ml/sec

The relative density of hydrogen $= D_1 = 1$

The relative density of $SO_2 = D_2 = \frac{64}{2} = 32$

or, $16/x = \sqrt{32}$

or, $16/x = 4\sqrt{2}$ or, $x = 4/\sqrt{2} = 2\sqrt{2}$ ml $= 2{\cdot}8284$ ml

26. *The rates of diffusion of CO_2 and O_3 are 0·29 and 0·271 respectively. If the relative density of CO_2 be 22 (H=1). Calculate the relative density of O_3*

Ans : Let the relative density of O_3 be d_2

The relative density of $CO_2 = d_1 = 22$

r_1 and r_2 be the rates of diffusion of CO_2 and O_3 respectively

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

$$\text{or, } \frac{0{\cdot}29}{0{\cdot}271} = \sqrt{\frac{d_2}{22}}$$

$$\text{or, } \sqrt{d_2} = \frac{0{\cdot}29 \times \sqrt{22}}{0{\cdot}271} = 0{\cdot}29 \times 4{\cdot}69 \times 3{\cdot}69$$

$$= 5{\cdot}02$$

$d_2 = (5{\cdot}02)^2 = 25{\cdot}2$ (approx).

27. *Equal volumes of hydrogen and oxygen require 24 and 96 seconds respectively to diffuse out of a porous wall. What is the molecular weight of oxygen ?*

Ans : Given the time of diffusion of H_2=24 sec (t_1) and that of O_2=96 sec (t_2) Applying Graham's law of diffusion,

$$\frac{t_1}{t_2} = \sqrt{\frac{D_1}{D_2}}$$

D_1 and D_2 are the vapour densities of H_2 and O_2 respectively.

or, $\frac{24}{96} = \sqrt{\frac{D_1}{D_2}}$

or, $\sqrt{D_2} = \frac{96}{24}\sqrt{D_1}$

or, $\sqrt{D_2} = \frac{96}{24}\sqrt{1} = 4$

$D_2 = (4)^2 = 16$

Hence the molecular weight of oxygen = 16 × 2 = 32.

28. *432 ml of a gas A takes 36 minutes to diffuse through a porous hole. 288 ml of another gas B takes 48 minutes to diffuse through the same porous hole under the same conditions of temperature and pressure. If the molecular weight of B=64 what is the molecular weight of A ?*

Ans : r_1 = rate of diffusion of $A = \frac{432}{36 \times 60} = 0{\cdot}2$ ml/sec

r_2 = rate of diffusion of $B = \frac{288}{48 \times 60} = 0{\cdot}1$ ml/sec

Applying Graham's Law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{0{\cdot}2}{0{\cdot}1} = \sqrt{\frac{64}{M_1}}$$

$$\therefore \quad \sqrt{M_1} = \frac{0{\cdot}1 \times \sqrt{64}}{0{\cdot}2} = \frac{0{\cdot}1 \times 8}{0{\cdot}2} = 4$$

or, $M_1 = 16$

The molecular weight of $A = 16$.

29. *100 ml of a gas mixture containing 10% CO_2 and 90% of another unknown gas is kept in a porous vessel. It is found that 100 ml of O_2 gas is diffused out of the vessel in 75 seconds. The gas mixture is diffused from the vessel in 86 seconds. If the relative density of oxygen be 16, find the molecular weight of the unknown gas.*

Ans : Let the rate of diffusion of $CO_2 = r_1$

,, ,, ,, ,, ,, $O_2 = r_2 = \frac{100}{75} = \frac{4}{3}$ ml/sec

,, ,, ,, ,, ,, the mixture $= r_3 = \frac{100}{86}$ ml/sec

Molecular weights of CO_2 and O_2 are 44 and 32 respectively. Hence from Graham's law :

$$\frac{r_1}{4/3} = \sqrt{\frac{32}{44}} \quad \text{or,} \quad \frac{3r_1}{4} = \sqrt{\frac{32}{44}} \quad \text{or,} \quad r_1 = \frac{4\sqrt{8}}{3\sqrt{11}}$$

or, rate of diffusion of $CO_2 = \frac{4\sqrt{8}}{3\sqrt{11}}$ ml/sec

Let x = Relative density of the unknown gas

∴ Relative density of the gas mixture

$$= \left[\frac{22 \times 10}{100} + \frac{90 \times x}{100}\right] = \frac{9x+22}{10}$$

$$\text{or,} \quad \frac{r_1}{r_3} = \sqrt{\frac{\text{Density of the gas mixture}}{\text{Density of } CO_2}} \quad \text{or,} \quad \frac{\frac{4\sqrt{8}}{3\sqrt{11}}}{\frac{100}{86}} = \frac{\sqrt{\frac{9x+22}{10}}}{\sqrt{22}}$$

or, $\dfrac{16\times8\times(86)^2}{(100)^2\times9\times11}=\dfrac{9x+22}{10\times22}$

or, $9x+22=\dfrac{16\times8\times86\times86\times220}{100\times100\times9\times11}$

or, $9x+22=210{\cdot}4$

or, $9x=188{\cdot}4$

or, $x=\dfrac{188{\cdot}4}{9}=20{\cdot}93$

$\therefore$ the density of the unknown gas$=20{\cdot}93$

$\therefore$ the molecular weight of the unknown gas$=20{\cdot}93\times2=41{\cdot}86$

30. *The time of diffusion of a gas mixture containing ozone and oxygen is 105 seconds and that of same volume of oxygen under the same condition of temperature and pressure is 100 seconds. Calculate the percentage by volume of ozone in the mixture if the relative density of ozone is 24.*

Ans : Let V ml of the gas be diffused out.

$\therefore$ Rate of diffusion of gas mixture of O_3 and $O_2=\dfrac{V}{105}$ ml/sec

Rate of diffusion of pure $O_2=\dfrac{V}{100}$ ml/sec

$d=$ Density of the mixture of the gases and the density of pure $O_2=16$.

or, $\dfrac{V/105}{V/100}=\dfrac{\sqrt{16}}{\sqrt{d}}$ or, $d=17{\cdot}64$

Let x be the percentage of O_3 in the gas mixture.

$\therefore$ % of $O_2=(100-x)$ and the density of the mixture is $17{\cdot}64$.

or, $x\times24+(100-x)16=17{\cdot}64\times100$

or, $8x=164$

or, $x=20{\cdot}5$

$\therefore$ The percentage of ozone in the gas mixture$=20{\cdot}5$.

31. *A mixture of 1·12 litre H_2 and 1·12 litre D_2 is kept at N.T.P. in a bulb. It is connected to a second bulb by a glass tube having a stopcock. The second bulb is completely evacuated. The stopcock is opened for some time and then is closed. It is observed that the first bulb now contains 0·05 g of H_2. Find the percentage of gas mixture by weight in the second bulb.* [*I.I.T. 1976*]

Ans : Weight of 1·12 litre of H_2 at N.T.P.$=\dfrac{2\times1{\cdot}12}{22{\cdot}4}=0{\cdot}1$ g

Weight of 1·12 litre of D_2 at N.T.P.$=\dfrac{4\times1{\cdot}12}{22{\cdot}4}=0{\cdot}2$ g

Let $M_1=$ Mol. wt. of H_2
$M_2=$ Mol. wt. of D_2
$r_1=$ rate of diffusion of H_2
$r_2=$ rate of diffusion of D_2

$$\therefore\ \frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}}=\sqrt{\frac{2}{1}}=\sqrt{2}$$

or, $r_1=\sqrt{2}\ r_2$

Let $V_1=$ Volume of H_2 gas diffused in time t
$V_2=$ Volume of D_2 gas diffused in time t

$\therefore\quad r_1=\dfrac{V_1}{t}$ and $r_2=\dfrac{V_2}{t}$

or, $\frac{V_1}{t} = \sqrt{2}\,\frac{V_2}{t}$

or, $V_1 = \sqrt{2}\,V_2$

According to the problem after sometime the first bulb contain 0·05 g of H_2

$\therefore$ $(0{\cdot}1 - 0{\cdot}05) = 0{\cdot}05$ g of H_2 is diffused in the second bulb. Volume of 0·05 g of H_2 at N.T.P. = 0·56 litre.

or, $V_2 = \frac{0{\cdot}56}{\sqrt{2}}$ litre

Weight of $D_2 = \frac{0{\cdot}2}{1{\cdot}12} \times \frac{0{\cdot}56}{\sqrt{2}} = 0{\cdot}0707$ g

Weight of total gas in the second bulb = Weight of diffused $H_2 + O_2$
$= 0{\cdot}05 + 0{\cdot}0707 = 0{\cdot}1207$ g.

$\therefore$ % of H_2 in the second bulb = 41·4%
% of D_2 in the second bulb = 58·6%

32. *A straight glass tube has two inlets x and y at the two ends. The lengths of the tube is 200 cm. HCl gas through inlet x and NH_3 gas through inlet y are allowed to enter the tube at the same time. White fumes first appear at a point P inside the tube. Find the distance P from x (HCl = 36·5, NH_3 = 17)* [*I.I.T. 1980*]

Ans : Let us assume that the air, NH_3 and HCl inside the tube are at same temperature and pressure.

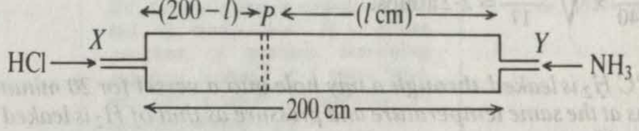


Fig 7·20

Hence the rates of the diffusion of the gases must be proportional to the distance crossed in the tube.

Let l = Distance in cm crossed by NH_3 gas

$\therefore$ $(200 - l)$ = Distance in cm crossed by HCl gas

$$\text{or,}\quad \frac{\text{rate of diffusion of } NH_3}{\text{rate of diffusion of HCl}} = \frac{\text{Distance crossed by } NH_3}{\text{Distance crossed by HCl}}$$

$$\text{Again,}\quad \frac{\text{rate of diffusion of } NH_3}{\text{rate of diffusion of HCl}} = \sqrt{\frac{\text{Mol. wt. of HCl}}{\text{Mol. wt. of } NH_3}}$$

$$\therefore\quad \frac{\text{Distance crossed by } NH_3}{\text{Distance crossed by HCl}} = \sqrt{\frac{\text{Mol. wt. of HCl}}{\text{Mol. wt. of } NH_3}}$$

$$\text{or,}\quad \frac{l}{200 - l} = \sqrt{\frac{36{\cdot}5}{17}} = 1{\cdot}465$$

or, $l = 293 - 1{\cdot}465\,l$

or, $l + 1{\cdot}465\,l = 293$

or, $2{\cdot}465\,l = 293$

or, $l = \frac{293}{2{\cdot}465} = 118{\cdot}9$ cm.

$\therefore$ Distance of P from $x = 200 - 118{\cdot}9 = 81{\cdot}1$ cm.

33. *At room temperature NH_3 gas at 1 atmosphere pressure and HCl gas at P atmosphere pressure are allowed to effuse through identical pin holes from opposite ends of a glass tube of 1 metre length and of uniform cross section. NH_4Cl is first* *formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of P ?* [*I.I.T. 1982*]

Ans :

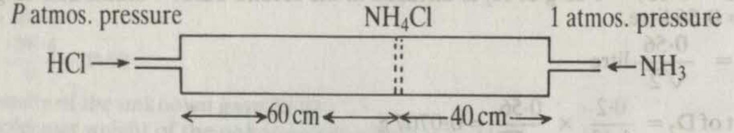


Fig 7·21 :

The time by which HCl gas crossed 60 cm in the tube, NH_3 crosses 100−60 = 40 cm distance

$$\therefore \frac{\text{Rate of diffusion of } NH_3}{\text{Rate of diffusion of HCl}} = \frac{40}{60}$$

Again at constant temperature the rate of diffusion of gas is directly proportional to the pressure but inversely proportional to the square root of molecular weight.

$$\text{or, } \frac{\text{Rate of diffusion of } NH_3}{\text{Rate of diffusion of HCl}} = \frac{\text{Pressure of } NH_3}{\text{Pressure of HCl}} \times \sqrt{\frac{\text{Mol. wt. of HCl}}{\text{Mol. wt. of } NH_3}}$$

$$\frac{40}{60} = \frac{1}{P} \times \sqrt{\frac{36·5}{17}}$$

$$\text{or, } P = \frac{60}{40} \times \sqrt{\frac{36·5}{17}} \simeq 2·2 \text{ atmos.}$$

34. *At 27°C H_2 is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of H_2 is leaked through the same hole for 20 minutes. After the effusion of the gases the mixture exerts a pressure of 6 atmos. The H_2 content of the mixture is 0·7 mole. If the volume of the container is 3 litres, what is the mol. wt. of the unknown gas ?* [*I.I.T. 1992*]

Ans : Vol. of the effused gas mixture at 27°C and 6 atmos pressure = 3 litres.

No. of mloes of the gas mixture = $\frac{PV}{RT} = \frac{6 \times 3}{0·082 \times 300} = 0·7317$

The H_2 content of the mixture = 0·7 moles

$\therefore$ The moles of the unknown gas = (0·7317 − 0·7) = 0·0317

Let M the mol.wt. of the gas then

$\frac{r_{H_2}}{r_g} = \frac{0·7/20}{0·0317/20} \quad \sqrt{\frac{M}{2}}$, where r_H and r_g are the rate of diffusion of H_2 and unknown gas respectively and M = mol.wt. of the unknown gas.

$$\text{or, } \frac{0·7}{0·0317} = \sqrt{\frac{M}{2}} \quad \text{Or, } M = 975·23$$

35. *The pressure in a bulb dropped from 2000 to 1500 mm of Hg in 47 minutes when the contained O_2 leaked through a small hole. The bulb was then completely evacuated. The mixture of O_2 and another gas of mol.wt. 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of Hg was introduced. Find the molar ratio of two gases remaining in the bulb after a period of 74 minutes.* [*I.I.T. '81*]

Ans : As the evacuated bulb contains a mixture of O_2 and another gas in the molar ratio of 1 : 1 at a pressure of 4000 mm, the partial pressure of each gas is 2000 mm.

The drop of pressure of O_2 after 47 minutes = (2000 − 1500) = 500 mm of Hg

$\therefore$ The drop of pressure of O_2 after 74 minutes = $\frac{500 \times 74}{47} = 787·2$ mm of Hg.

$\therefore$ After 74 minutes the pressure of O_2 will be
$= 2000 - 782{\cdot}2 = 1212{\cdot}8$ mm of Hg.

Let the rate of diffusion of other gas be r_g

$$\therefore \frac{r_g}{r_o} = \sqrt{\frac{32}{79}}$$

$\therefore$ The drop of pressure for the other gas $= 787{\cdot}2 \times \sqrt{\frac{32}{79}} = 501{\cdot}8$ mm of Hg.

$\therefore$ The pressure of other gas after 74 minutes $= 2000 - 501{\cdot}8 = 1498{\cdot}2$ mm

$$\text{molar ratio} = \frac{\text{moles of other gas}}{\text{moles of } O_2} = \frac{1498{\cdot}2}{1212{\cdot}8} = \frac{1{\cdot}24}{1} = 1{\cdot}24 : 1$$

• Statement of different laws of gases and their mathematical formula are tabulated below for the convenience of students :

Laws	Statement	Mathematical expression
1. Boyle's Law	At constant temperature, the volume of a definite mass of a gas is inversely proportional to pressure of the gas.	$V \propto \frac{1}{P}$ When T is constant or, $V = K/P$ or, $PV = K$ constant
2. Charles' Law	At constant pressure the volume of a definite mass of a gas increases or decreases by 1/273 of its volume at 0°C for each degree celsius rise or, fall in temperature at constant pressure or pressure remaining constant, volume of a given mass of a gas is directly proportional to absolute temperature.	$V_t = V_0\left(1 \pm \frac{1}{273}\right)$ and $V \propto T$ at constant P or, $V/T = K$
3. Dalton's Law of Partial Pressure	At constant temperature, when 2 or more non reacting gases or vapours are mixed together in a vessel of fixed volume, the total pressure of the mixture of gases or vapours is the sum of the partial pressure of individual gases	If P = total pressure of the mixture and p_1, p_2, p_3 etc., be the partial pressure of individual gases then $P = p_1 + p_2 + p_3 + \cdots \cdots$
4. Graham's Law of Diffusion	Under similar conditions of temperatemperature and pressure, rates of diffusion of two gases are inversely proportional to the square root of their relative densities.	$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$

• Exercises •

1. Mention the characteristics of gaseous states of matter.

2. State Boyle's law. Explain the law with the help of two graphs. *[W.B.H.S. '92]*

3. Express Boyle's law and Charle's law in the form of equation.

4. Deduce the definition of absolute Zero from Charles' law.

5. State Charles' law. The pressure is changed on a fixed mass of a gas at constant temperature. Show the nature of variation of the product of pressure and volume (PV) against pressure by means two separate graphs only. *[W.B.H.S. '89]*

6. Prove that at constant pressure, the volume of a given mass of gas is directly proportional to the absolute temperature. *[W.B.H.S. '83]*

Deduce the equation $PV = RT$, why is this equation called molar gas equation ? At N.T.P. write down the values of P, V and T in C.G.S unit and hence find out the value of molar gas constrant in C.G.S. unit. *[W.B.H.S. '84]*

7. Stating the units of *P*, *V* and *T* find the value of *R* in litre atmosphere unit. *[W.B.J.E. '87] [W.B.H.S. '86]*

8. Deduce the equation $PV = nRT$. Why *R* is called universal gas constant ? *[W.B.H.S. '91]*

9. What do you mean by the partial pressure of gases ?
State and explain Dalton's law of partial pressure. *[W.B.H.S. '82, 86]*

10. State and illustrate grahams law of diffusion with examples. *[W.B.H.S. '83, 88]*

11. Establish the equation $PV = nRT$ with the help of Boyles' law and Charles' law. *[W.B.H.S. '84]*

12. What is meant by diffusion ? State grahams law of diffusion. Give an example of its practical application. *[W.B.H.S. '87]*

13. Deduce the values of *R* in calories per Kelvin per mole. *[W.B.H.S. '86]*

14. Establish the relation between temprature, pressure and volume of a given mass of gass. State the laws from which the said relation is obtained.

15. What do you mean by absolute Zero. How does the volume of a gas depend in it ? Is it possible to have a temperature below absolute Zero ? What happens when a gas is cooled to absolute Zero ?

16. Deduce the equation of state (a) for 1 mole (b) for *n* mole and for *w* g of a gas.

17. What is meant by molar gas constant ? Why is it known as universal gas constant ? Give its value in different units ?

18. Deduce an expression between the partial pressure of a gas mixture and the total pressure exerted by the gas mixture. What is aqueous tension ?

19. Explain why H_2 diffuses more rapidly than CO_2. Arrange the following gases in order of increasing rate of diffusion—CO_2, SO_2 and CO.

20. What is meant by effusion. What is the difference between effusion and diffusion ? State the law which gives the rate of diffusion.

State how will you determine the molecular wt. of a gas with the help of diffusion.

21. Describe the nature of graph obtained in the following cases—
(ii) '*V*' is Plotted against '*T*' at constant pressure,
(ii) '*PV*' is plotted against '*P*' at constant temperature.

Objective type questions :

1. 5g of each of the following gases at 27°C and 750 mm pressure are taken. Which of them will have the least volume ?
(a) HF, (b) HCl, (c) HBr, (d) HI *[Ans. (d)][MLNR '91]*

2. If the absolute temperature of a gas is doubled and the pressure is reduced to one-half, the volume of the gas will
(a) remain unchanged (b) be doubled (c) increase four-fold (d) be reduced to 1/4th *[Ans. (c)]*

3. Under constant pressure, a certain gas at 0°C was cooled until its volume was reduced to one-half. The temperature at this stage is (a) 0 (b) −136·5K (c) −136·5C (d) −273°C *[Ans. (c)]*

4. Equal wts of CH_4 and O_2 are mixed in an empty container at 25°C. The fraction of the total pressure exerted by O_2 is (a) 1/3 (b) 1/2 (c) 2/3 (d) 1/3 × 273/298 *[Ans. (a)][I.I.T. '81]*

5. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called—
(a) critical temp. (b) Boyle temp. (c) inversion temp. (d) Reduced temp. *[Ans. (b)][I.I.T. '83]*

6. The rate of diffusion of methane of given temperature is twice that of a gas X. The molecular weight of X is (a) 64, (b) 32, (c) 4, (d) 8. *[Ans. (a)] [I.I.T. '90]*

7. Rate of diffusion of a gas is
(a) directly proportional to its density, (b) directly proportional to its mol. wt. (c) directly proportional to the square of its mol. wt. (d) inversaly proportional to square root of its mol. wt. *[Ans. (d)] [I.I.T. '85]*

8. If a gas is expanded at constant temperature, (a) the pressure decreases (b) the KE of the molecules remain same (c) KE of the molecules decreases (d) the number of molecules of the gas increase. *[Ans. a, b] [I.I.T. '86]*

9. A bottle of dry NH_3 and a bottle of dry HCl connected through a long tube are opened simultaneously at both ends, the white ring of NH_4Cl first formed will be (a) At the centre of the tube (b) near the HCl bottle (c) near the NH_3 bottle (d) throughout the length of the tube. *[Ans. (b)][I.I.T. '86]*

10. In Vander Waals equation for a real gas, the temperature that accounts for inter molecular forces is (a) $(V - b)$, (b) RT, (c) $\left(P + \frac{a}{V^2}\right)$, (d) $(RT)^{-1}$ *[Ans. (c)] [I.I.T. '88]*

11. Two gases mix with each other to form a homogeneous mixture. This phenomenon is called—
(a) effusion, (b) addition, (c) synthesis, (d) diffusion *[Ans. (d)]*

12. Equal weight of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is
(a) 1 : 2, (b) 1 : 1, (c) 1 : 16, (d) 15 : 16 *[Ans. (d)] [I.I.T. '93]*

13. At constant volume, for a fixed number of moles of a gas the pressure of the gas increases with the rise of temperature due to

(a) Increase in average molecular speed, (b) increased rate of collisions among molecules, (c) increased molecular attraction, (d) decrease in mean free path. [***Ans.*** (a)] *[I.I.T. '92]*

14. According to Kinetic theory of gases, for a diatomic molecule—

(a) The pressure exerted by the gas is proportional to the mean velocity of the molecule, (b) the pressure exerted by the gas is proportional to the roof mean square velocity of the molecule, (c) the roof mean square velocity of the molecule is inversely proportional to the absolute temp, (d) the mean translational Kinetic evergy of the molecule is proportional to the absolute temp. [***Ans.*** (d)] *[I.I.T. '91]*

15. Fill up the blanks—

(a) Under similar conditions of temperature and pressure the rates of diffusion of gases vary —— as the square roots of their —— or ——. *[I.I.T. '86]*

(b) Smell of cooking gas during leakage from the gas cylinder is detected because of the properties of ——.

(c) The vapour density of a diatomic gas is 25, its atomic weight is ——.

(d) The value of PV for 5.6 litre of an ideal gas is —— RT at NTP. *[I.I.T. '82]*

(e) The rate of diffusion of a gas is —— proportional to both —— and square root of molecular mass. *[I.I.T. '86]*

(f) The total number of electrons present is 18 ml of water is ——.

(g) The volume of an ideal gas becomes zero at —— K.

- **Numerical problems :**

1. A gas occupies 300 cc at 27°C and 760 mm pressure. Calculate the volume of the gas at normal temperature and pressure. [***Ans.*** 273 cc] *[W.B.H.S '89]*

2. The volume of a certain amount of gas becomes 1·3 litre from 1 litre when its temperature is increased from 0°C to 83°C at constant pressure. From this result deduce the value of absolute zero in celsius. [***Ans.*** 273·3°C] *[W.B.H.S. '85]*

3. A vessel of 120 ml capacity contains a certain mass of a gas at 20°C and 750 mm pressure. The gas is transferred to a vessel whose volume is 180 ml. Calculate the pressure of the gas at 20°C. [***Ans.*** 500 mm]

4. What volume of air will be expelled from a vessel containing 400 ml at 7°C when it is heated to 27°C at the same pressure ? [***Ans.*** 28·57 ml]

5. The weight of 350 ml of a diatomic gas at 0°C and 2 atomspheric pressure is 1 g. Calculate the weight in gram of one atom. [***Ans.*** $2{\cdot}65\times10^{-23}$] *[I.I.T. '70]*

6. What is the volume of 6 g of H_2 at 1·5 atoms and 273°C ? [***Ans.*** 44·8 litres] *[I.I.T. '74]*

7. How much air will escape from a flask of 1 litre capacity if it is heated from 25°C to 35°C, the pressure remaining constant. [***Ans.*** 33·56 ml]

8. A gas expands from 1 litre to 1·128 litre when it temperature is increased from 0°C to 35°C at constant pressure. From this data calculate the value of absolute zero in celsius. [***Ans.*** 273·4°C]

9. Spherical baloon contains a gas at 27°C and 1 atoms. pressure. How much additional pressure is to be applied to compress the gas in order to make it fill another spherical baloon of 1/4th diameter of the first at the same temperature ? [***Ans.*** 63 atoms.]

10. A gas contracts from 1 litre to 0·6313 litres due to a fall of temperature from 0°C to −100°C the pressure remaining the same. From this result calculate the value of absolute zero in celsius. [***Ans.*** 271·2°C]

11. At 273K and 1 atmospheric pressure a gas occupies 2·5 litres. Calculate its volume at 546°C and 150 cm pressure of Hg. [***Ans.*** 3·8 litres]

12. Calculate the decrease in volume of a baloon, whose volume is 450 ml at 12°C and 756 mm pressure of Hg when it is taken into the bottom of a mine where the pressure is 765 mm and temperature is 5°C. [***Ans.*** 16·5 ml]

13. Oxygen is present in 1 litre flask at a pressure of $7{\cdot}6\times10^{-10}$ mm of Hg. Calculate the number of O_2 molecules present in the flask at 0°C. [***Ans.*** $2{\cdot}69\times10^{10}$]

14. A flask of capacity 100 ml contains some vapour at 23°C. It is then evacuated to 10^{-3} mm of Hg. Calculate the number of molecules left in the flask. [***Ans.*** $3{\cdot}26\times10^{15}$]

15. 0·64 g of a gas occupies 224 ml at 76 cm pressure and at 273 K temperature. At what temperature 1 g of the gas will occupy 1 litre at 1 atmospheric pressure ? [***Ans.*** 507°C] *[W.B.H.S. '91]*

16. The density of a gas is found to be 2·07 g per litre at 30°C and 2 atmospheric pressure. What is its density at S.T.P. ? [***Ans.*** 1·15 g/litre]

17. 0·44 g of a colourless oxide of nitrogen occupies 224 ml at 1520 mm Hg and 273°C. Identify the compound. How much in gram does one molecule of this compound weigh ? [***Ans.*** N_2O, $7{\cdot}26\times10^{-23}$] *[I.I.T. '71]*

18. 0·1 g of a volatile substances on vaporisation displaced 27 ml of moist air measured at 15°C and 740 mm pressure. Calculate the molecular weight of the substance. (Aqueous tension at 15°C = 12·7 mm). [***Ans.*** 91·46]

19. A gas occupies 0·418 litre at 27°C and 740 mm pressure. Calculate— (i) its volume at N.T.P., (ii) If the weight of the same gas is 3·0 g find the molecular weight of the gas, (iii) If the mass of the gas is increased to 7·5 g in the same vessel and the temperature is lowered to 280 K, what would be the pressure now ? [***Ans.*** 0·3703 litre, 181·4, 2·272 atmos]

20. 50 ml of H_2 at S.T.P. were introduced into a tube of cross section 1·2 cm^2 and standing on a trough of mercury. The height of the gas inside the tube was observed to be 15 cm. The pressure is brought down to 750 mm and the temperature is increased to 31°C. Find the height of the gas contained in the tube under this conditions. [***Ans.*** 15·3 cm]

21. The volume of a gas together with a solid substance occupies 150 ml at 1 atmosphere pressure. When the pressure is increased to 1000 mm of Hg, the combined volume becomes 116·4 ml. Calculate the volume of the solid substance. Temperature remains constant. [***Ans.*** 10 cm^3]

22. A desicator of internal volume 1 litre and containing N_2 at 1 atmosphere pressure is partially evacuated to a final pressure of 7·6 mm of Hg, while the temperature remains constant. What is the volume of the gas at this stage ? [***Ans.*** 1 litre] *[I.I.T. '76]*

23. There are 0·003 moles of H_2 and 6×10^{-5} moles of water vapour in a sample of H_2 collected on water in gas jar at 1 atmosphere pressure. Calculate the partial pressure of H_2 and water vapour. [***Ans.*** H_2 = 745 mm, water vapour = 15 mm]

24. A gas mixture at 760 mm pressure of Hg contains 80% nitrogen and 20% oxygen. Find at the partial pressure of each gas. [***Ans.*** P_{N_2} = 608 mm, P_{O_2} = 152 mm] *[W.B.J.E.E. '85]*

25. 1 g hydrogen and 4 g oxygen are kept in a vessel of capacity 20 litre at 27°C. Calculate the total pressure inside the vessel and the partial pressures of hydrogen and oxygen. [***Ans.*** PH = 0·615, PO = 0·1537 P = 0·768 atmos]

26. The total pressure of a mixture of 1 g of H_2 and 10 g of CO is 800 mm. Calculate the partial pressure of each of the gases in the mixture. [***Ans.*** H_2 = 466·7 mm, CO = 333·329 mm]

27. At S.T.P. a gas mixture of three gases A, B and C contains 77% of A, 21% of B and 1·5% of C by volume. Determine the partial pressures of A, B and C. [***Ans.*** P_A = 585·2 mm, P_B = 159·6 mm P_C = 11·4 mm]

28. 45 g of electrolyte gas is contained in a 60 litre gas holder at 0°C. Find the partial pressure of each constituent. Find the total pressure. [***Ans.*** H_2 = 0·933 atmos, O_2 = 0·467 atmos, total = 1·4 atmos]

29. At 100°C a closed vessel of capacity 1500 ml contains 0·4 g of O_2 and 0·6 g of H_2. What is total pressure of the gas mixture in the vessel ? [***Ans.*** P = 6·37 atmos] *[W.B.H.S. '92]*

30. A mixture of 2 g of hydrogen and 8 g of oxygen is kept in a container of capacity 20 litres at 27°C. Find the partial pressure of each gas. [***Ans.*** H_2 = 1·231 atmos, O_2 = 0·307 atmos]

31. A glass vessel of capacity 2 litre contains nitrogen and water vapour in equimolecular proportions at 10^{-3} mm pressure of Hg at 303 K. Calculate— (i) total number of moles of N_2 and H_2O present, (ii) total mas of the gaseous mixture when the mixture is cooled to 50°C. [***Ans.*** No of moles of N_2 & H_2O = $5{\cdot}29\times10^{-8}$, Total mass = $2{\cdot}43\times10^{-6}$ g]

32. A two litre glass vessel contains N_2 and water vapour in equimolecular proportions at a pressure of 10^{-3} mm of Hg at 303 K. Calculate— (i) the number of moles of N_2 and water vapour present, (ii) total mass of the gaseous mixture. Find the mass of the gas when the mixture is cooled to −50°C. [***Ans.*** (i) 5×10^{-3}, (ii) $24{\cdot}33\times10^{-7}$ g, (iii) $14{\cdot}81\times10^{-7}$ g] *[I.I.T. '72]*

33. Calculate the root mean square velocity of Hg atoms having kinetic energy of 1000 cal mole^{-1}. (At. wt. of Hg = 200) [***Ans.*** $2{\cdot}04\times10^4$ cm sec^{-1}]

34. Calculate R.M.S. velocity of O_3 molecules at 27°C and 740 mm pressure. [***Ans.*** 39032·57 cm/sec] *[I.I.T. '85]*

35. Using Vander Waals' equation, Calculate the pressure exerted by 44 g of CO_2 when it occupies a volume of 0·05 litres at 100°C (a = 3·592 atmos litre^2 mol^{-2}, b = 0·04267 litre mole^{-1}, R = 0·0821 litre atmos K^{-1} mole^{-1}). [***Ans.*** 2741 atmos]

36. A gaseous hydrocarbon contains 14·28% of H_2. The rates of diffusion of H_2 and this hydrocarbon are $1:\sqrt{14}$. Calculate the formula of the hydrocarbon. [***Ans.*** C_2H_4]

37. 96 ml of O_3 diffuse through an orifice. Under same conditions of temperature and pressure 100 ml of CO_2 diffuses through the same orifice in the same time. If the molecular wt. of CO_2 is 44 find that of O_3. [***Ans.*** 47·74]

38. 100 ml of H_2 take 20 minutes to diffuse out a vessel. How long will it take to 40 cc of O_2 under similar conditions ? [***Ans.*** 32 minutes]

39. 1 litre of N_2 weighs 1·25 g and 1 litre of Cl_2 weighs 3·21 g under same conditions of temperature. Calculate the relative rates of diffusion of the two gases. [***Ans.*** 1 : 1·16]

40. 432 ml of a gas A takes 36 minute to effuse through a fine hole. 288 ml of another gas B takes 48 minute to pass out of the same hole under same conditions of temperature and pressure. The molecular wt. of B is 64. Find out the molecular wt. of A. [***Ans.*** 40] *[W.B.H.S. '87]*

41. A cylinder of 10 litres capacity contains oxygen under a pressure of 20 atmosphere at 27°C, is leaking at a constant rate of 5 ml of O_2 per minute at N.T.P. Calculate the fall of pressure inside the cylinder at the end of 10 hours. [***Ans.*** 0·33 atmos]

42. 114 ml of H_2 diffuses in the same time as 29·4 ml of an unknown gas. Find the density of the unknown gas. [*Ans.* 15·035]

43. The molecular weights of two gases are 64 and 100. The rate of diffusion of the first one is 15 ml per second. Find the rate of diffusion of the second gas. [*Ans.* 12 ml Sec^{-1}] */W.B.H.S. '90/*

44. One litre of a gaseous mixture is effused in 5 minutes 11 seconds, while 1 litre of O_2 takes 10 minutes. The gaseous mixture contains CH_4 and H_2. Calculate (a) density of the mixture (b) percentage by volume of each gas in the mixture. [*Ans.* 4·3, $CH_4 = 47{\cdot}14\%$, $H_2 = 52{\cdot}86\%$]

45. At constant temperature, 250 ml of N_2 at 760 mm pressure and 500 ml of O_2 at 600 mm pressure are put together in a litre flask. What will be the final pressure of the mixture ? [*Ans.* 490 mm]

46. Small amounts of NH_3 and hydrogen chloride are released simultaneously at the opposite ends of a 2 m long tube. At what point the formation of NH_4Cl would start ? [*Ans.* 0·81 m from the end of HCl]

47. There is an air bubble with radius of 0·5 cm at the bottom of a lake where the temperature is 7°C and pressure is 280 k Pa. It rises to the surface where the temperature is 27°C and the pressure is 100 k Pa. What is the radius of the air bubble when it reaches the surface ? (Given 1 Atmos = 101·325 k Pa) [*Ans.* 0·72 cm]

48. 500 cc of O_2 diffuse through a porous partition in 20 seconds. How long will it take to diffuse out 200 cc of CO_2 through it ? [*Ans.* 9·4 seconds]

49. A flask can withstand a pressure up to 1·6 atmosphere. It is filled with Cl_2 at 283 K and 764 mm pressure. At what temperature the flask would explode if the temperature is gradually increased ? [*Ans.* 177·43°C]

50. At 27°C hydrogen is leaked through a tiny hole into a vessel for 10 minutes. Another unknown gas at the same temperature and pressure as that of hydrogen is leaked through the same hole for 10 minutes. After the effusion of the gases the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0·35 mole. If the volume of the container is 1·5 litres, what is the molecular weight of the unknown gas ? [*Ans.* 1008·2]

SOLUTION AND SOLUBILITY

8

When two or more non reacting substances are intimately mixed together, two types of mixtures result—(i) **Homogeneous mixture** and (ii) **Heterogeneous mixture.** In homogeneous mixture the constituent particles are mixed in such a way that the physical properties of each part of the mixture remains the same. This is called **true solution.** On the other hand when the constituent particles do not mix uniformly, the mixture is called heterogeneous mixture.

8.1. Solution.

A homogeneous mixture of two or more non reacting substances is called solution. The composition of a solution is uniform throughout. Though a solution is a mixture, the relative amounts of the ingredients may be changed within certain limits. Formation of a solution is purely physical process having a single phase system, although thermal change may take place during its preparation, i.e., the process of dissolution may be exothermic or endothermic. On the basis of the above idea.

- *A true solution is a single phase perfectly homogeneous mixture of two or more components (solids, liquids or gases) such that their relative amounts may be varied within certain limits.*

The composition, physical and chemical properties of a solution remains the same in every part of it.

When two substances are mixed, the homogeneous material thus obtained is known as **binary solution**. A solution consisting of three substances is called **ternary solution** and so on.

Solute : *The component of the solution present in smaller proportion is called solute.*

Solvent : *The component of the solution present in larger proportion is called solvent, the phase of which determines the phase of the solution.*

Thus the relation between solute, solvent and solution can be expressed as.

Solution = Solute + Solvent

- **Types of solutions based on three states of matter :**

Depending upon the state of the solute and that of the solvent, there may be the following types of solutions.

State of solvent		State of the solute	Examples of solutions
(1) Solid	+	solid	Different types of alloys such as Brass (Cu + Zn).
		liquid	Amalgam (Hg + Zn). (Hg + Au)
		gas	H_2 occluded in palladium.
(2) liquid	+	liquid	Water + ethanol
		solid	Water + common Salt
		gas	Water + CO_2 i.e., Soda water
(3) Gas	+	gas	Air—Solution of $N_2 + O_2$
		liquid	Moisture present in air
		solid	Smoke—air and carbon particles.

• Characteristics of Solution :

A solution behaves differently from the solute and the solvent from which it is formed. These characteristics are however physical. Sometime dissolution of a solute in a solvent is a chemical one e.g., Dissolution of $Fe(CN)_2$ in aqueous KCN solution when Fe^{++} loses its chemical properties.

(i) The molecules of the solute or the ions formed by the dissolution of the polar solutes mix with the solvent intimately. Hence the composition and physical properties of the solution remain same in all parts of the solution.

(ii) The particles of the solute in the solution is too small to be visible even under powerful microscope (The diameter of the solute particles is about 10^{-8} cm in a solution).

(iii) The solute can not be separated from the solution even by filtration or by gravitational force.

(iv) No significant changes of the physical properties of the solute and solvent are observed in solution although minute changes are noted.

(v) The relative amounts of both the solute and the solvent may be gradually increased or decreased within a certain fixed limit.

(vi) The solute and the solvent from the solution are separated by evaporation, crystallisation etc.

(vii) The colour of the aqueous solution is controlled by the nature of the solutes. The colour of a solution containing an ionic solute depends upon the ions given by the polar solutes and the colour of the solution containing non polar solute depends upon the molecules of the solutes. KNO_3, sugar, alcohols are colourless hence their aqueous solutions are also colourless. The violet colour of an aqueous solution of $KMnO_4$ is attributed to the violet colour of MnO_4^- ions present in aqueous medium. Similarly copper sulphate solution is blue because $[Cu(H_2O)_4]^{++}$ ions are blue coloured.

(viii) Colligative properties of the solutions e.g., **vapour pressure, osmotic pressure, boiling point, freezing point** etc., are determined by the concentration of the solution i.e., depend upon the relative amount of the solute and the solvents.

(ix) Dissolution of a solute in a solvent may be either exothermic or endothermic.

8.2. Similarities and dissimilarities between solution and compound.

A compound registers a number of similarities with a solution despite of the fact that the latter is a mixture.

Similarities : (i) A solution is a homogeneous mixture of solute and solvent. A chemical compound is also homogeneous.

(ii) Just like the formation of a chemical compound the formation of a solution is always accompanied by thermal change.

(iii) Unlike mixture, the constituents of a chemical compound must be present in a definite proportion by weight, so also the relative amounts of the solute and the solvents are fixed in a saturated solution. Thus, 39 g of NaCl dissolve in 100 g of water at 100°C. More than this quantity of NaCl (39 g) would not dissolve in 100 g of water at this temperature.

(iv) A compound has fixed melting and boiling points. The boiling and melting points of a saturated solution are also constant.

Dissimilarities : Despite of a number of similarities, a solution is called a mixture not a compound. This is because of the fact that—

(i) The constituent particles (solutes) in a solution retain their chemical properties.

(ii) The solutes in a solution can be separated by such easy means like crystallisation, distillation, evaporation etc. The constituent particles of a chemical compound can not be separated by such processes.

(iii) The relative quantities of the constituent particles of a solution at a definite temperature can be varied to a certain limit. The limit can be increased by increasing the temperature. But the relative proportions of the constituent particles of a chemical compound can not be changed.

(iv) Heat may be evolved or absorbed in the preparation of solution. This is known as heat of solvation which is not of chemical origin since no new compound is formed when a solute dissolved in a solvent.

8.3. Classification of solution according to concentration.

Depending upon concentration, solution is divided into 3 classes—(i) **Unsaturated** (ii) **Saturated** and (iii) **Super saturated.**

(i) **Unsaturated solution :** When one spoonful of sugar is added to a glass of water and the mixture is stirred, the sugar dissolves in water completely. The solution thus produced is unsaturated as the solution can dissolve more sugar with the increase of its density. Such a solution is called unsaturated solution.

- *The solution, in which more quantity of solute can be dissolved at a particular temperature is called unsaturated solution.* In fact all dilute solutions are unsaturated.

(ii) **Saturated solution :** On gradual addition of sugar to a constant volume of water with continuous stirring, a time comes when the sugar does not dissolve inspite of vigorous stirring. Some sugars are left undissolved at the bottom of the beaker at room temperature, i.e., the water in the beaker is unable to dissolve this quantity of sugar any more. The clear homogeneous solution thus formed above the undissolved sugar is called saturated solution of sugar at that temperature. At this stage the sugar in the solid state is in equilibrium with the sugar in solution i.e., the rate at which sugar dissolves, is equal the rate at which the dissolved sugar crystallises at that temperature. The density of a saturated solution does not alter inspite of adding more sugar to the solution.

- *A solution is said to be saturated at a fixed temperature, when the maximum quantity of solute which a solvent can dissolve at that temperature, is present in the solution. The density of such solution does not change on addition of solute.*

• Preparation of saturated solution :

About 100 ml of water are taken in a 250 ml beaker. A few grams of blue vitriol crystals are added to it and stirred with a glass rod. The blue vitriol crystals dissolve and the solution turns blue. The process is continued and a time will come when the rate of dissolution becomes so slow that even on prolonged stirring a considerable amount of blue vitriol is left undissolved at the bottom of the beaker. The clear solution from above is transferred to another beaker. This is a saturated solution of blue vitriol at room temperature.

• Effect of temperature on saturated solution :

A saturated solution of blue vitriol of room temperature is heated and some more crystals of blue vitriol are added to it. It is observed that the newly added blue vitriol dissolves in the solution. Now the temperature of the solution is kept constant and the addition of blue vitriol crystals and stirring are continued. A time will come when the solution will not be able to dissolve any more blue vitriol, the later will remain undissolved at the bottom of the beaker. The solution thus formed is also a saturated solution of blue vitriol at increased temperature.

Thus, saturation of a solution is a function of temperature. A saturated solution becomes unsaturated on raising the temperature of the solution i.e., the capacity to dissolve more solute is enhanced. This explains why temperature must be *mentioned* in case of *mentioning* a saturated solution.

The quantity of the solute in a saturated solution is fixed if temperature and pressure remain constant.

- **Method of converting an unsaturated solution into a saturated one.** Three methods are available to convert an unsaturated solution (Solution of solid in liquid) into a saturated solution.

(i) On adding more amount of solute into the solvent.

(ii) On cooling the solution, the later becomes saturated at a particular temperature.

(iii) On evaporation of the solvent, the quantity of solvent in the solution decreases but the solute remains constant. When the solution is brought back to the previous temperature, it becomes saturated.

(iii) **Super saturated solution :** At constant temperature and pressure the quantity of solute in a saturated solution is constant. On increasing the temperature, however, the capacity of a saturated solution to dissolve more solute is increased. As a result if more solute is added to that solvent it dissolves. But if the solution is brought back to the previous temperature the excess solute comes out of the solvent. Sometimes it is observed that the excess solute which was dissolved in the solvent at an elevated temperature does not separate out even if the solution is cooled slowly. This solution is known as **super saturated** solution and the state is referred to *super saturation*.

Thus *a solution is said to be supersaturated which contains a greater proportion of the solute than it contained in a saturated solution at that temperature. The solution is unstable and the solute separates out from such solution on agitation by stirring or seeding with crystals. In fact a super saturated solution represents a system in a meta-stable condition.*

428 g of sodium thiosulphate (hypo) $Na_2S_2O_3, 5H_2O$ are dissolved in 100 g of boiling water to form a saturated solution. If this hot solution is cooled to room temperature, some hypo will separate out from the solution, since the solubility of a substance decreases with the lowering of temperature. Now if this hot and clear solution of hypo is carefully poured into a clean glass test tube and its mouth is covered with a cotton, it is observed that inspite of cooling the solution to room temperature the solute does not separate out from the solution in the form of crystals. This is a supersaturated solution of hypo at room temperature. It contains 428 g of hypo in 100 g of water. Saturated solution of hypo contains 84·5 g of hypo per 100 g of water at room temperature. Now if a small crystal of hypo is added to this super saturated solution of hypo, ions of the solution will begin to attach themselves to form the crystals and there will be an increase in the amount of solid hypo.

- **Identification of saturated, unsaturated and super saturated solution at a particular temperature :**

Addition of excess of solute to a solution leads to its identification—

(i) If on addition of the solute to a solution, the density of the solution increases, then it is proved that the given solution is unsaturated.

(ii) A saturated solution does not dissolve any more solute. Hence when excess solute is added to it, the later is left undissolved at the bottom of the solution and the density of the solution does not alter inspite of the addition of more solute.

(iii) If the concentration (density) of the solution decreases by the addition of a piece of the solute to a solution, then it is proved that the solution is super saturated solution. The particles grows in size in such solution.

- **Relation between saturated, unsaturated and super saturated solution.**

(i) The solution which can dissolve more solute with the increase of its density, is called unsaturated solution.

(ii) The solution which can not dissolve more solute and whose density does not alter inspite of adding solute to it, is called saturated solution.

(iii) The solution which may be forced to dissolve excess of solute by changing the environment is called super saturated solution. The density of such solution is decreased on addition of a piece of solute.

8.4. State of equilibrium between the solvent and solute in a solution.

Whenever a solute is added to a solvent at a particular temperature, the ions of the polar solute or molecules of the non polar solute begins to detach from the surface of the solid solute, and diffuse freely in the solvent forming a homogeneous solution. At the beginning there will be a few solid molecules in the solvent of the solution and the solution will be dilute. This process of dissolution continues till the dissolved particles of the solute in the solution start a reverse process of returning back from the solution to the surface of the undissolved solute i.e., few solute molecules in solution strike the solid and deposit on its surface.

Due to the kinetic energy possessed by the particles of the solute, they are in constant random motion in the solution. As a result some of them collide with the other particles and they strike the undissolved solute and may remain attached to it. The larger the number of solute particles in the solution, the greater is the possibility of collision of the particles with the solid crystals. At constant temperature the number of solute particles which leave the solid and go into the solution in each second per square cm of surface area, remains constant. The number of solute particles that leave the solution and are deposited on the solid solute in each second will increase, as the number of solid particles in a given volume of solution increases.

Ultimately a time comes when the rate of dissolution becomes just equal to the number of solute particles return back from the solution. At this instant no further increase in concentration is observed and a state of equilibrium is attained between the solute in crystal and in solution. This is a state of dynamic equilibrium because although the amount of crystals in the solid state and the particles of solute in solution does not change, the rate of dissolution of the solute and the reverse process of crystallisation of the particles in solution remains same. Under the circumstances the solution thus formed is called a saturated solution at that temperature.

$$\boxed{\text{Ions or particles of the solute}} \rightleftharpoons \boxed{\begin{array}{l}\text{Ions or particles of}\\ \text{the dissolved solute}\\ \text{in the solution}\end{array}}$$

However, if the temperature is altered, the above state of equilibrium is disturbed. Hence *a saturated solution is a solution where the ions or particles of the dissolved solute in solution is in equilibrium with those of undissolved solute at a fixed temperature. A solution, where this equilibrium has not yet reached is called an unsaturated solution.*

A super saturated solution is a state of unstable equilibrium rather a metastable one since here more solute is dissolved at a fixed temperature.

8.5. Mechanism of dissolution of a solute in a liquid—Water is a versatile solvent.

It depends upon the nature of both solute and solvents. The axiom "*Like dissolves like*" predicts the solubility of a substance in a particular solvent. Thus (1) **polar solutes are soluble in polar solvents** and (2) **Non-polar solutes are soluble in non-polar solvents.**

[A] **Solubility of polar solute in polar solvent (e.g. NaCl in water) :**

Ionic compounds are soluble in polar solvents but not in non-polar solvents. Thus NaCl is soluble in water but insoluble in benzene. This is because of the fact that the solvent molecules attract the ions of the crystals, pull them apart from the crystal lattice and forms solvated ions. These solvated cations and anions must be more stable than the ions in the crystal lattice. Formation of solvated ions means that there must be some strong forces between the ions of the solute and the solvent molecules. *Whenever solvation of the ions takes place, some energy is released which is called solvation energy which results from the ion-solvent interaction. Solvation energy of the ions in a polar solvent is usually high and low in non polar solvent.* As a general rule *if the solvation energy of the ion exceeds the lattice energy of the crystal then that crystal will be soluble in that solvent. If lattice energy of the crystal is greater than that of solvation energy, then that solute will be insoluble in it.* Since solvation energy of ions of NaCl in water is higher than the lattice energy of NaCl crystal, the latter is soluble in water but solvation energy of NaCl crystal in non-polar solvent like benzene is comparatively low and is much less than the lattice energy of NaCl, hence it is insoluble in non-polar solvent like benzene.

[Lattice energy of a crystal is defined as the energy released when the gaseous cation and anions are brought together from infinite distance to the equilibrium distance to form one gram mole of ionic crystal

$$\underset{(g)}{M^+} + \underset{(g)}{X^-} \rightarrow \underset{\substack{\text{(1 gm mole}\\ \text{of solid)}}}{M^+X^-} + \underset{\text{(Lattice energy)}}{\text{Energy released}} \quad]$$

Thus, it is obvious that the energy which must be provided for the separation of the ions from the crystals is derived from the solvation of ions. Let us now examine how NaCl, is brought into aqueous solution and the different parameters that causes the process of dissolution of NaCl.

It is known that the attractive forces between an ion and a neutral molecule is strong if the molecule has high dipole moment or high polarisability and high dielectric constant. Larger the dipole moment, stronger is the attraction of the molecule by the ion and high is the solvation energy. Again with the increase of the polarisability of the solvent molecules, solvation energy also increases. Therefore a solvent with high dipole moment and dielectric constant is better to dissolve ionic compound than a solvent with lower value of dipole moment or dielectric constant. Water possesses these two qualities.

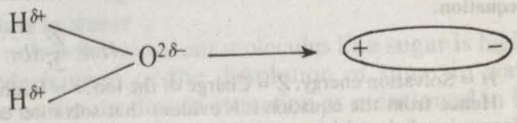


Fig 8.1 : Water is a polar molecule

Water has a larger dipole moment of 1·84 Debye. Since the difference of electronegativity between H and O atom is high, the electron pair between the O–H bond is shifted towards oxygen atom. As a result O develops $O^{\delta-}$ charge and each hydrogen atom $H^{\delta+}$ charge i.e., positive (formal) charge is developed on two hydrogen atoms and negative (formal) charge on oxygen atom. Whenever NaCl crystal is put into water, the positively charged Na^+ ion is attracted by negatively charged oxygen atom of water molecule to form ion-dipole interaction. Similarly the negatively charged Cl^- ion is attracted by the positively charged hydrogen atoms of water molecule through ion-dipole interaction. The attractive forces holding the ions Na^+ and Cl^- are diminished because of high dielectric constant of water molecule. Na^+ and Cl^- ion become hydrated and fly apart.

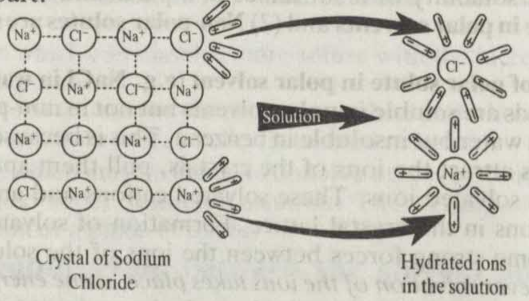


Fig 8.2 : The mechanism of dissolution of ionic compound, (NaCl)

As a result of this process, the *solvation energy* (In case of water, solvation energy is called *hydration energy*) is released which in this case is much greater than the lattice energy of NaCl and the crystal structure of NaCl is raptured and goes into aqueous solution.

$$Na^+ + xH_2O \rightleftharpoons [Na(H_2O)_x]^+ + Q_1 \text{ cals}$$
$$Cl^- + yH_2O \rightleftharpoons [Cl(H_2O)_y]^- + Q_2 \text{ cals}$$
$$\therefore Na^+ + Cl^- + (x+y)\, H_2O \rightleftharpoons [Na(H_2O)_x]^+ + [Cl(H_2O)_y]^- + [Q_1 + Q_2]$$

$Q_1 + Q_2$ = Hydration energy or solvation energy

Again the energy required to separate two ions is decreased if the attractive forces between them are less. The attaractive forces between ions depend upon the dielectric constant of the medium. According to Coulomb's Law,

$$F = \frac{1}{\epsilon} \cdot \frac{q_1 q_2}{r^2}$$

F = force that attracts the two oppositely charged ions
q_1 and q_2 = charges of the two ions respectively.
r = distance between the two ions.
ϵ = dielectric constant of the medium.

The delectric constant of water is 78·54. This means whenever NaCl comes in contact with water, the attractive forces between Na^+ and Cl^- in water becomes $\frac{1}{78 \cdot 54}$ times if they were in vacuum.

Thus the attractive forces between Na^+ and Cl^- ions are considerably diminished which also facilitates the process of dissolution.

[The relation between the solvation energy and dielectric constant of the solvent is given by **Born equation.**

$$H = \frac{Z^2}{2r} \left(1 - \frac{1}{\epsilon}\right)$$

H = Solvation energy, Z = Charge of the ion, r = Radius of the ion, ϵ = dielectric constant.

Hence from the equation it is evident that solvation energies and solubilities of salts increase with increasing dielectric constant of the medium.]

Dielectric constant and dipole moment of some solvents are given below for comparison

Solvents	Dipole moment in Debye	Dielectric constant
Water	1·84	78·54
Liquid NH_3	1·46	22 (−33·5°C)
Liquid HF	1·9	83·6
Liquid SO_2	1·61	17·27

[Last but not the least, solvation of a salt in a solvent is governed by the polarisation effect. In fact solubility is dependent of the relative polarisability of the anions and of the solvent molecule. The solubility of the salt is usually low if the polarisation power of the cations is large and the polarisability of the anions is high. But if the solvent molecule is easily polarisable then the solubility of the salt will increase. Thus the solubility of $AgCl$, $PbCl_2$, $HgCl_2$ in water is low but the solubility of KCl, $NaCl$, $NaBr$ in water is high. This is because of the fact that the polarisation power of Ag^+, Pb^{++} is much higher than that of K^+, Na^+ and water is less polarisable than the halides. The dipole moment of NH_3 is lower than H_2O but NH_3 is more polarisable than H_2O. Hence $AgCl$, $HgCl_2$ etc., are soluble in NH_3.]

[For Polarisation and Polarisability see Fajan's rule in Vol. II]

[B] Dissolution of polar covalent solute in polar solvent :

The competition between the Lattice energy of the ionic solid and the solvation energy of the ions results in the solubility of ionic crystals in polar solvents like water which is characterised by high dipole moment as well as high dielectric constant. The polar covalent molecules e.g., HCl, HBr etc., are also soluble in polar solvents like water. Although they do not possess any ions but contains formal positive and negative charges. As the difference of electronegativity between the two atoms increases the bond polarity also increases. Whenever this type of polar covalent molecule comes in contact with water, the negative end of water attracts the positive end of polar covalent molecule and the negative end of the molecule is being attracted by the positive end of the dipole water. This force of attraction is sufficient to weaken the force of attraction between the positive and negative end of the polar molecule, finally the polar covalent bond is ruptured leading to the solvation of the covalent molecules and finally its dissolution. This is evidenced by the reaction of water with hydrogen chloride to produce ionisation

$$x\mathrm{HCl} + x\mathrm{H_2O} + x\mathrm{H_2O} \rightleftharpoons [\mathrm{H_3O}]^+_x + [\mathrm{Cl(H_2O)}]_x$$

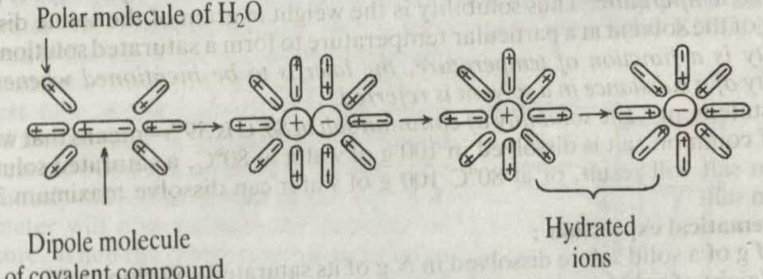
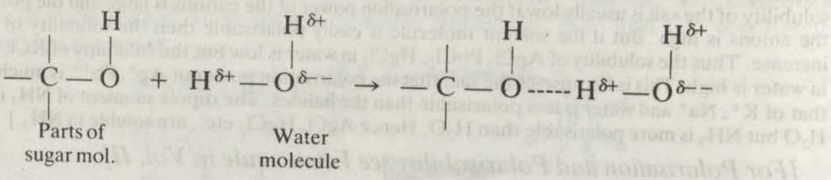


Fig 8.3 : The mechanism of dissolution of polar covalent compound in water.

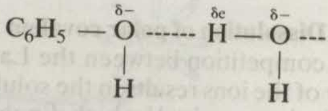
[C] Dissolution of non-polar solute in water :

It is a common experience that non-polar covalent molecules like sugar is highly soluble in polar solvent water. Mechanism of the dissolution of sugar in water cannot be explained by ion-dipole or dipole-dipole attraction as mentioned in the previous section. Here a new approach, called hydrogen bond between water and –OH group of sugar is responsible for its solubility. The O–H bond is polar because of wide difference of electronegativity between oxygen and hydrogen atom. The $H^{\delta+}$ point of H_2O molecule acts as a bridge between the two oxygen atoms (one of –OH of sugar and the other –OH of water) giving rise to associated molecules. The solubility of *Ethyl alcohol, Methyl alcohol* in water is also attributed to the hydrogen bonding between alcohol and water. In fact any organic compound which has polar group like $-NH_2$, $-OH$ etc., are soluble in water due to hydrogen bond with water.



$$-\underset{|}{\overset{|}{C}}-\overset{\overset{H}{|}}{O} + H^{\delta+}-\overset{\overset{H^{\delta+}}{|}}{O^{\delta-}} \rightarrow -\underset{|}{\overset{|}{C}}-\overset{\overset{H}{|}}{O}\text{-----}H^{\delta+}-\overset{\overset{H^{\delta+}}{|}}{O^{\delta-}}$$

Hydrogen bond between phenol and water—



$$C_6H_5-\underset{\underset{H}{|}}{\overset{\delta-}{O}}\text{------}\overset{\delta c}{H}-\underset{\underset{H}{|}}{\overset{\delta-}{O}}\text{---}$$

- **Dissolution of non-polar solutes in non-polar solvents :**

Non-polar compounds dissolve in non-polar solvents. Thus **methane** dissolves in **carbon tetrachloride** but neither CH_4 nor CCl_4 is soluble in water. Although non-polar molecules are held together by inter moleculer forces, the molecular particles possess vibrational movements. The non-polar solvent molecules are also in constant motion. When the non-polar solute is kept in contact with the non-polar solvent, the solute-solvent molecules start attracting by new inter molecular forces. If this force is large enough to tear off the molecule of solute, then the process of dissolution of non-polar solute in non-polar solvent begins. Thus the intermolecular forces of attraction between the solute and solvent molecules must exceed that between solute molecule. At this condition the solute dissolves in the solvent. Thus the solubility of Methane in Carbon-tetrachloride is attributed to the existence of stronger force between the molecules of Methane and Carbon tetrachloride molecules than that present among the molecules of Methane or Carbon tetrachloride.

8.6. Solubility.

- *The solubility of a solute in a solvent at a particular temperature is defined as the number of gram of the solute which is necessary to saturate 100 gram of the solvent at the that temperature.* Thus solubility is the weight in gram of the solute dissolved in 100 g of the solvent at a particular temperature to form a saturated solution. Since *solubility is a function of temperature, the later is to be mentioned whenever the solubility of a substance in a solvent is referred.*

The statement *"The solubility of common salt at 80°C is 39"*—means that when 39 gram of common salt is dissolved in 100 g of water at 80°C, a saturated solution of common salt will result, or at 80°C 100 g of water can dissolve maximum 39 g of common salt.

Mathematical expression :

Let M g of a solid solute dissolved in N g of its saturated solution at t°C

$\therefore$ Weight of solvent $= (N-M)$ g

$\therefore$ $(N-M)$ g of solvent dissolve M g of solute at t°C

$\therefore$ Solubility of the solute at $t°\text{C} = \dfrac{M\times 100}{N-M}$

or, $\text{Solubility} = \dfrac{100\times \text{weight of solute in g}}{\text{Weight of solvent in g}}$

8.7. Determination of solubility.

(i) **To find the solubility of a substance in a liquid at room temperature.**

Some distilled water is taken a beaker and pure sodium chloride is added pinch by pinch into it with constant stirring with a glass rod. Addition of solid NaCl and stirring with glass rod are continued till some solid remains undissolved. Temperature of the solution is recorded with a thermometer. Let the temperature be t°C. Let the solution be kept for sometime. 25 ml of this saturated solution is pipetted out and transferred into a previously weighed porcelain basin. The basin with NaCl solution is weighed again. Now the NaCl solution is evaporated by placing the basin over water bath. White solid NaCl is found to be left in the basin. It is completely dried by placing it in an air oven and cooled in a desiccator and weighed. The processes of drying in air oven and cooling in desiccator are continued till a constant weight is found.

Calculation : Let the temperature of the room = t°C. The weight of dry procelain basin = W g. Weight of saturated NaCl solution + basin = W_1 g

$\therefore$ Weight of saturated NaCl solution = $(W_1 - W)$ g

Again at the end of the experiment,

Weight of basin + dry NaCl salt = W_2 g

$\therefore$ Weight of dry salt = $(W_2 - W)$ g

Weight of water = $(W_1 - W) - (W_2 - W)$ g

$= (W_1 - W_2)$ g

Now at t°C $(W_1 - W_2)$ g of water dissolve $(W_2 - W)$ g of sodium chloride to form a saturated solution.

$\therefore$ 100 g of water dissolve $\dfrac{100 \times (W_2 - W)}{(W_1 - W_2)}$ g of sodium chloride to form a saturated solution.

$\therefore$ Solubility of Sodium chloride at t°C = $\left[\dfrac{100 \times (W_2 - W)}{W_1 - W_2}\right]$

The solubility of $CuSO_4$, KNO_3 KCl etc., at room temperature can be found out by the above method.

(i) **To determine the solubility of a substance at a temperature higher or lower than the room temperature.**

The weights of some dry porcelain basins are taken in a chemical balance water is boiled in a hard glass test tube and solid KNO_3 is added pinch by pinch into the boiling water with constant stirring with a stirrer until some solid KNO_3 is left undissolved in the solution. The clear supernatant liquid is a saturated solution of KNO_3 at 100°C.

The test tube is then placed into hot water contained in a beaker. A thermometer is dipped into the test tube and the solution in the test tube is continuously stirred as shown in the Fig. 8·4. Thermometer will now indicate the decrease of temperature. When the temperature is reduced to 80°C. Some more solid KNO_3 will be crystallised out. The supernatant liquid is a saturated solution of KNO_3 at 80°C. As soon as temperature is 80°C 10 ml of the clear solution from the top are taken out quickly by means of pipette and is transferred to a previously weighed porcelain basin and its weight is recorded. The solution is evaporated to dryness on a water bath. It is completely dried in air oven, cooled in a desiccator and weighed.

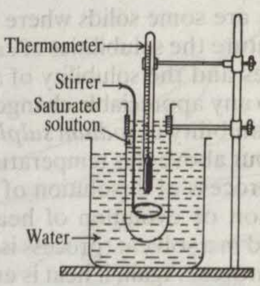


Fig 8.4 :

Calculation :

Let the weight of empty basin = W g

Weight of basin + KNO_3 solution = W_1 g

Weight of KNO_3 solution = $(W_1 - W)$ g

Weight of basin + solid KNO_3 = W_2 g

$\therefore$ Weight of solid KNO_3 = $(W_2 - W)$ g

Weight of water = $(W_1 - W) - (W_2 - W)$ g

$= (W_1 - W_2)$ g

The temperature of the saturated solution = 80°C. So the weight of KNO_3 dissolved in 100 g of water at 80°C

$$= \frac{100\,(W_2 - W)}{(W_1 - W_2)}\ \text{g}$$

$$\therefore \text{ Solubility of } KNO_3 \text{ at } 80^\circ C = \left[\frac{100\,(W_2 - W)}{(W_1 - W_2)}\right]$$

In this way the solubility of KNO_3 at different temperatures namely 70°C, 60°C, 50°C, 40°C etc., can be calculated. In order to find the solubility of KNO_3 at temperature less than room temperature, the test tube is to be placed on freezing mixture and process is repeated i.e., drawing 10 ml of saturated solution and transferring it in a previously weighed basin, weighing, evaporating the solution to dryness and further weighing of the basin with dried salt as described earlier.

8.8. Influence of temperature and pressure on the solubility of solids in liquids.

The solubility of a solid in a liquid depends upon the temperature. The solubility of a solid in liquid is so intimately related, that the temperature must be mentioned whenever the solubility of any solute is expressed. Generally the solubility of a solid in a liquid increases with the rise of temperature e.g., the solubility of potassium nitrate in water is 65 at 40°C but at 50°C its solubility is increased to 85. Solubilities of lead nitrate, magnesium sulphate, ammonium salts, potassium chloride etc., in water, are found to increase with the increase of temperatures.

It has been found that solubilities of different solids in the same solvent may not increase to the same extent with the rise of temperatures, e.g., the solubility of KNO_3 increases very quickly with the increase of temperatures than that of potassium chlorate.

There are some solids where the reverse trends are noted, e.g., with the rise of temperature the solubilities of *calcium sulphate, calcium oxalate, calcium hydroxide* decreases and the solubility of *sodium chloride* or *potassium dichromate* does not undergo any appreciable change.

The solubility of *sodium sulphate* first increases with the rise of temperature upto 32·4°C but above this temperature its solubility sharply decreases.

The process of dissolution of a solute in a solvent is always attended with either absorption or evolution of heat. Normally if heat is absorbed when a solute is dissolved in a solvent (process is endothermic) its solubility increases with the rise of temperatures. Again if heat is evolved during the dissolution of a solute in a solvent (process is exothermic) its solubility decreases with the increase of temperatures.

Pressure has practically no influence on the solubility of a solid solute in a liquid solvent.

8.9. Solubility curve.

The solubility of a solid in a liquid varies with the temperatures. This variation can be represented by plotting solubility against temperature on a graph paper. Such a graph is commonly known as "*solubility curve*". To draw such curves, at first the solubilities of say KNO_3 and NaCl are determined at different temperatures. The solubility values at different temperatures are recorded in the following table—

Potassium Nitrate		Sodium Chloride	
Temperature (°C)	Solubility	Temperature (°C)	Solubility
10	20	10	34
20	32	20	35
30	45	50	36
40	65	80	39
50	85		
70	138		

Temperature is plotted along X-axis and solubility along Y-axis. 1 unit in graph paper along X-axis = 10°C and 1 unit along Y-axis = 10 g. The solubility curves are shown in Fig (8:5).

• Nature and significance of solubility curve :

A look at the Fig 8·7 reveals that the solubility of most of the solids increases with the rise of temperatures. Since the rate of increase of solubility of a solid depends upon its nature, different solids will register increase of solubility with the increase of temperatures to different degrees.

Some curves are highly steep, some are less and some are almost parallel to X-axis, the increase of solubility being less marked.

(i) The solubility curves of solids like KNO_3, $NaNO_3$ show a steep rise with increase of temperatures. This shows that the solubilities of these solids increase rapidly with rise of temperatures.

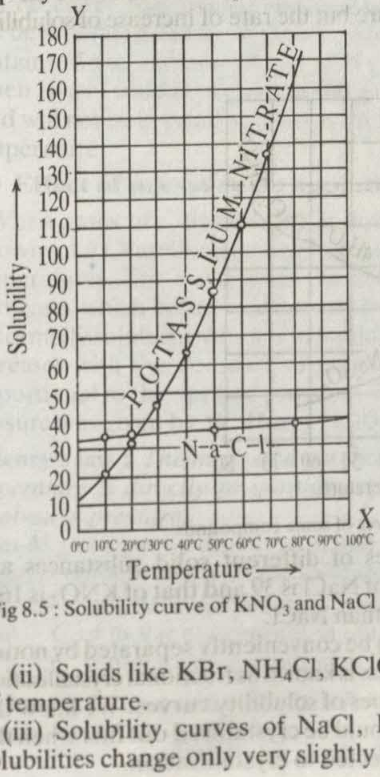


Fig 8.5 : Solubility curve of KNO_3 and NaCl

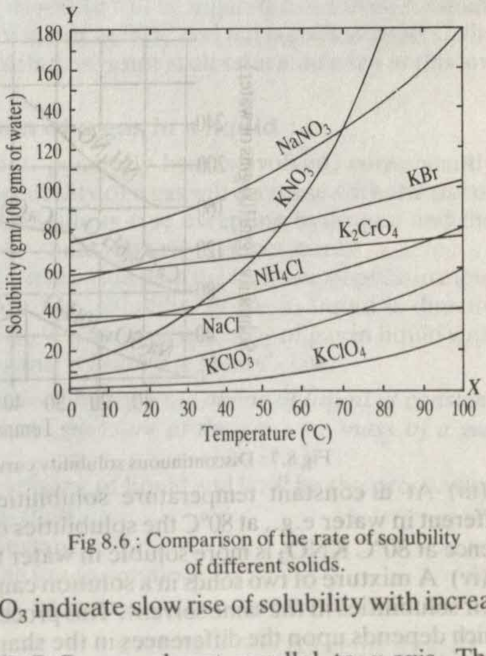


Fig 8.6 : Comparison of the rate of solubility of different solids.

(ii) Solids like KBr, NH_4Cl, $KClO_3$ indicate slow rise of solubility with increase of temperature.

(iii) Solubility curves of NaCl, K_2CrO_4 are almost parallel to *x*-axis. Their solubilities change only very slightly with the rise of temperature.

(iv) Cerous sulphate $Ce_2(SO_4)_3$ shows a decrease of solubility with the increase of temperatures.

(v) Discontinuous curves are observed for NH_4NO_3, hydrated salts like $CaCl_2$, $6H_2O$ and Glauber's salt (Na_2SO_4, $10H_2O$)—the study of the last one is worth noting. This discontinuity is always due to the change in the composition of the solid. The discontinous curve for NH_4NO_3 is attributed to a polymorphic change from β-rhombic form to α-rhombic form at the transition temperature of 32°C. In case of $CaCl_2$, $6H_2O$, the discontinuity is due to the formation of $CaCl_2$, $4H_2O$ at 30°C and $CaCl_2$, $2H_2O$ at around 48°C. Different polymorphic forms or different hydrates are stable over a certain temperature range. Glauber's salt Na_2SO_4, $10H_2O$ registers an increase of solubility markedly upto 32·38°C but its solubility after this, decreases with the rise of temperatures. At the transition temperature 32·38°C it releases 10 molecules of water and becomes anhydrous Na_2SO_4, so the solubility of latter part is in fact the solubility of anhydrous sodium sulphate and not of Na_2SO_4, $10H_2O$. There are, in fact, two solubility curves for two solutes—one for hydrated and the other for anhydrous salt.

- **Utility of solubility curve :**

(i) The study of the solubility curve of a solid indicates its solubility at different temperatures. Hence without performing any actual experiment we can find the solubility of a substance at different temperatures simply by observing the solubility curve. Thus Fig 8·6 records the solubility of KNO_3 at 45°C = 75.

(ii) The rate of change of solubility with the temperature is recorded in the solubility curve. Thus in Fig 8·7 we see that the solubilities of NH_4Cl and KNO_3 increase rapidly with the increase of temperature but the rate of increase of solubility of NH_4NO_3 is less than that of KNO_3.

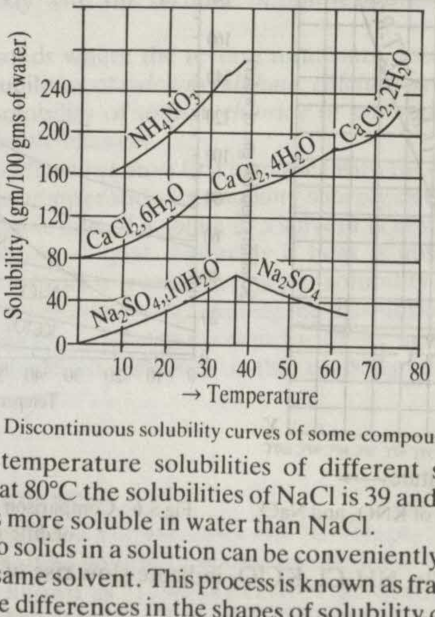


Fig 8.7 : Discontinuous solubility curves of some compounds.

(iii) At a constant temperature solubilities of different solid substances are different in water e.g., at 80°C the solubilities of NaCl is 39 and that of KNO_3 is 160. Hence at 80°C KNO_3 is more soluble in water than NaCl.

(iv) A mixture of two solids in a solution can be conveniently separated by noting their solubilities in the same solvent. This process is known as fractional crystallisation which depends upon the differences in the shapes of solubility curves. We know the solute having less solubility between the two would be crystallised out first when the saturated solution containing two solids is subjected to crystallisation.

Record of solubility curve suggests that at 100°C KCl is more soluble in water than $KClO_3$. Hence when an aqueous solution containing KCl and $KClO_3$ is evaporated at 100°C and cooled slowly, it will be saturated first by $KClO_3$. On further cooling solid $KClO_3$ will separate out from the solution and finally $KClO_3$ will be completely separated out from the mixture. The mother liquor will contain KCl.

(v) If a hot saturated solution of known concentration be cooled to a given temperature then the weight of solutes to be thrown out of the solution as crystals can be readily obtained from a study of solubility curve. For example the solubility of KNO_3 at 70°C is 138 and at 30°C is 45. If a saturated solution of KNO_3 in 100 g of water at 70°C be cooled to 30°C, then $(138-45) = 93$ g of KNO_3 will be separated out from solution as crystals.

(vi) The solubility curve, in reality, indicates two states of a solution. The lower part indicates the condition for getting unsaturated solution of the solute while the upper part shows the condition for super-saturated solution or saturated solution containing an equilibrium between solvent and excess undissolved solute. Fig 8.8 shows the solubility curve of a 70 gram solute at 100 g water at 90°C. If we represent the graph through the point *C*, it will show an unsaturated solution. If we now reduce the temperature to 60°C and draw the graph through *B*, the solution will be saturated. If the temperature is further cooled to 30°C and represent the solubility curve through *D*, then the solution will be either super-saturated or excess solid will be separated out from the solution as crystals. Graph shows at 30°C the solution contains 35 g solute and $70-35 = 35$ g of solute will be separated out from solution. When 10 g of solid is present in 100 g of water at 90°C and if it is cooled to 30°C, the solid will not be crystallised out as the solution is not at all saturated even at this low temperature.

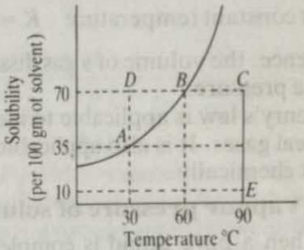


Fig 8.8 : Solubility curve exhibits two states of a solution.

- **Effect of pressure on a solution of a gas in a liquid :**

When gases are dissolved in a liquid, generally heat is evolved, consequently following Le Chatelier's principle the solubility of a gas will decrease with the rise of temperatures. For most gases the above rule is true excepting hydrogen and the inert gases which behave differently over same ranges of temperatures.

Normally solubility of a gas in liquid is increased with the increase of pressure and decreases with the decrease of pressure i.e., solubility of gas in liquid is directly proportional to the applied pressure. The variation of solubility of gas in liquid with pressure was given by **W. Henry** (1803) and is known as Henry's law.

Henry's law : *The mass of a gas dissolved by a given volume of liquid at constant temperature is directly proportional to the pressure of the gas i.e., mass of a gas dissolved ∝ pressure.*

Let M g of a gas be dissolved in unit volume of liquid and let P be the pressure of the gas at equilibrium with the solution, then,

$M \propto P$ or, $M = KP$ where K is constant.

Let C_s = molar concentration of the gas in solution.

C = molar concentration of the gas.

From ideal gas equation $P = XRT$. or, $P = CRT$. (as n/V = concentration C)

and $M \propto C_s$ or, $M = K_1 C_s$, K_1 constant.

Again $K = M/P = K_1C_s/CRT$.

Now when temperature remains constant, $\dfrac{C_s}{C} = \dfrac{KRT}{K_1} = \text{const.}$

$\therefore$ When temperature remains constant, the ratio of the molar cencentration of the gas in the solution and in gas itself is constant. This may be regarded as another form of Henry's law.

A third statement of Henry's law may be deduced as follows—

Let m g of a gas occupy V ml., M = molar mass of the gas.

For n moles of idal gas we get $PV = nRT$

$$\text{or,}\ PV = \frac{m}{M}RT \qquad \text{or,}\ m = \frac{MPV}{RT}$$

$$\text{Again,}\ K = \frac{m}{P} = \frac{MPV}{PRT} = \frac{MV}{RT}$$

$$\text{At constant temperature}\quad K = \frac{MV}{RT} \quad \text{or,}\ V = \frac{KRT}{M} = \text{constant.}$$

Hence, the volume of a gas dissolved in a definite volume of a liquid is independent of the pressure.

Henry's law is applicable to ideal gas only. Hence it is applicable at low pressure for real gases. It is also applicable to those gases which do not ionise or associate or react chemically.

• Vapour pressure of solutions and Raoult's law :

When a pure liquid is completely covered with a bell jar, a part of the liquid evaporates and fills up the space above the liquid surface with its vapour. At a particular temperature after sometime an equilibrium is reached between the vapour and liquid phases.

The vapour pressure of a liquid is the pressure exerted by the vapour in equilibrium with the liquid phase at a particular temperature.

When a non volatile solute is added to a liquid solvent to make a solution, the vapour pressure of the solution becomes less than that of the pure solvent.

Causes of lowering of vapour pressure :

According to Maxwell's distribution law, in a liquid, the molecules have different kinetic energies and they move with different velocities. Molecules having greater energies overcome the cohesive force and leave the surface of the liquid. In this way the liquid is evaporated. *The larger is the number of escaping molecules from the surface of the liquid, the larger will be the vapour pressure of the liquid.*

When a non volatile solute B is added to a solvent A, a solution is formed. Now in this solution the molecules of B also occupy some space on the surface of the liquid and thus the number of molecules of A on the surface is reduced. So the number of the solvent molecules ready to escape from the surface of the solution becomes less. As a result the partial vapour pressure of the solvent in solution becomes less than the vapour pressure of the pure solvent.

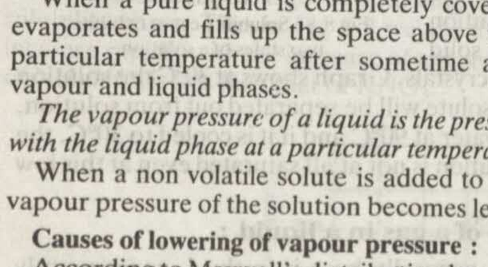


Fig 8.9 : Causes of lowering vapour pressure of a solution.

Raoult's law : Raoult's law expresses a relation between the partial vapour pressure of a component and its mole fraction in the solution. It is stated as—

- *For a solution of volatile liquids, the partial vapour pressure of a component of a solution is directly proportional to the mole fraction of that component.*

Let in a solution of two miscible liquid components A and B have their mole fractions X_A and X_B respectively. The partial vapour pressures of A and B are P_A and P_B respectively. Then according to Raoult's law—

$$P_A \propto X_A \quad \text{and} \quad P_B \propto X_B$$

In case of mixtures of two miscible liquids, Raoult showed that the above relation may be expressed as—

$$P_A = P_A{}^{\circ} X_A \quad \text{and} \quad P_B = P_B{}^{\circ} X_B$$

where $P_A{}^{\circ}$ and $P_B{}^{\circ}$ are the vapour pressures of pure components A and B respectively.

A plot of P_A against X_A or P_B against X_B for a solution should be a straight line according to Raoult's law. (St. lines I and II as shown in the fig. 8.10). These lines pass through points $P_A{}^{\circ}$ and $P_B{}^{\circ}$ when X_A or X_B equals to unity.

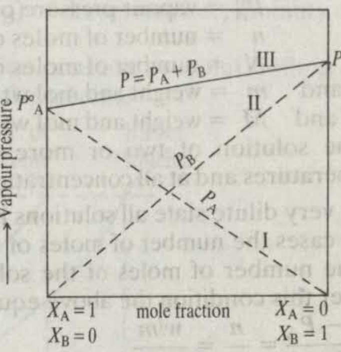


Fig 8.10

The total vapour pressure of the solution $P = P_A + P_B$ which is shown in the fig. as line—III which joins the points $P_A{}^{\circ}$ and $P_B{}^{\circ}$. The solutions which obey Raoult's law are called **ideal solutions.** The vapour pressures for such solutions are in between the values of $P_A{}^{\circ}$ and $P_B{}^{\circ}$ and all of them be on the straight line joining $P_A{}^{\circ}$ and $P_B{}^{\circ}$.

- **Solutions of non voiatile solute :**

Let us consider a solution produced by adding a non volatile solute to a volatile solvent, e.g., glucose and water. In such type of solution the vapour pressure of the solution is due to the solvent alone—the solute has no contribution to the vapour pressure of the solution. Consequently, in such case the total vapour pressure will be equal to the vapour pressure of the solvent in the solution. As a result, if mole fraction of a solvent in a solution is decreased, the vapour pressure of the solution will also decrease.

The total vapour pressure $P = P_A = P_A{}^{\circ} \times X_A$

For a binary mixture, $X_A + X_B = 1$

$$\text{or,} \quad X_A = 1 - X_B$$

$$\therefore \quad P_A = P_A{}^{\circ} X_A$$

$$\text{or,} \quad P_A = P_A{}^{\circ}(1 - X_B)$$

$$\text{or,} \quad \frac{P_A}{P_A{}^{\circ}} = (1 - X_B) \qquad \text{or,} \quad 1 - \frac{P_A}{P_A{}^{\circ}} = X_B$$

$$\therefore \quad \frac{P_A{}^{\circ} - P_A}{P_A{}^{\circ}} = X_B$$

Where $(P_A{}^{\circ} - P_A)$ = lowering of vapour pressure on the formation of solution.

$\frac{P_A{}^{\circ} - P_A}{P_A{}^{\circ}}$ = relative lowering of vapour pressure of the solution.

For nonvolatile solute, Raoult's law may be stated as follows—

- *The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute when the solvent alone is volatile.*

Mole fraction of the solute is defined as the ratio of number of moles of solute to the total number of moles in soln.

i.e., $$\frac{P_A^0 - P_A}{P_A^0} = \frac{n}{n+N} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}}$$

Where, P_A = vapour pressure of the solution.
P_A^0 = vapour pressure of the pure solvent.
n = number of moles of the solute.
N = number of moles of the solvent.
w and m = weight and mol wt. of the solute respectively.
W and M = weight and mol wt. of the solvent respectively.

The solution of two or more components which obey Raoult's law at all temperatures and at all concentrations is known as ideal solution.

In very dilute state all solutions have a tendency to behave like an ideal soln. In such cases the number of moles of the solute (n) becomes very small as compared to the number of moles of the solvent (N). Consequently ($n + N$) becomes N. Under this condition the above equation may be expressed as

$$\frac{P^\circ_A - P_A}{P^\circ_A} = \frac{n}{N} = \frac{w/m}{W/M}$$

This eq. is used to determine the molecular weight of a dissolved solute when the weight of the solvent and the relative lowering of vapour pressure of the solvent in solution are known.

• Colligative properties of solution

The properties of solution which depend on the number of particles of the solute and of the solvent, are known as colligative properties of solution.

The colligative properties of solution are—

(1) **Lowering of vapour pressure,** (2) **The elevation of boiling point,** (3) **The depression of freezing point,** (4) **Osmotic pressure.**

(1) **Lowering of vapour pressure :**

According to Raoult's law—$P_A = P_A{}^\circ X_A$

Where P_A = Vapour pressure of the solvent in a solution,
$P_A{}^\circ$ = Vapour pressure of the pure solvent
X_A = Concentration expressed in mole fraction of the solvent.

$$\text{i.e., } X_A = \frac{\text{mole of solvent}}{\text{moles of solute} + \text{moles of solvent}} = \frac{\text{mole of solvent}}{\text{Total number of moles}}$$

As mole fraction is a ratio, it has no unit.

(2) **The Elevation of boiling point :**

It is known to us that vapour pressure of a liquid increases with the rise of temperature and when the vapour pressure of the liquid becomes equal to the atmospheric pressure, the liquid begins to boil.

The vapour pressure of a solution is less than the vapour pressure of the pure solvent. As a result, the temperature at which the vapour pressure of a solution becomes equal to the atmospheric pressure, becomes higher than the actual boiling point of the pure solvent. Thus the presence of a solute in a solvent raise the boiling point of the solvent.

It has been observed that the elevation of boiling point of a solvent is directly proportional to the number of moles of the solute present in a definite amount of solvent.

$$\triangle T_b \propto m$$

or, $\triangle T_b = K_b . m.$ ....(1)

where, $\triangle T_b$ = elevation of B.P.

m = number of moles of solute in 1 kg (1000 g) of the solvent i.e., molality of the solute.

K_b = constant—called boiling point elevation constant or molal boiling point elevation constant or ebullioscopic constant of the solvent.

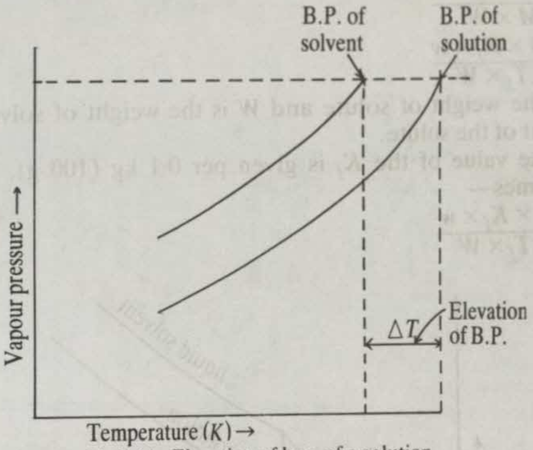


Fig 8.11 : Elevation of b.p. of a solution.

The equation (1) may be expressed as—

$$\triangle T_b = \frac{1000 \times K_b \times w}{M \times W}$$

$$\text{or, } M = \frac{1000 \times K_b \times w}{\triangle T_b \times W}$$

Where w is the weight of solute and W is the weight of solvent and M is the molecular weight of the solute.

Sometimes the value of the K_b is given per 0·1 kg (100 g). In such case the expression becomes—

$$M = \frac{100 \times K_b \times w}{\triangle T_b \times W}$$

(3) **The depression of freezing point :**

A liquid freezes at a temperature when its vapour pressure becomes equal to its solid phase. At the freezing point of a solvent, its solid and liquid phases are in equilibrium. Solvent (liquid) $\rightleftharpoons$ Solvent (solid).

Now on addition of a solute to a solvent, the vapour pressure of the solvent is lowered, which disturbs the equilibrium, liquid $\rightleftharpoons$ solid. At the freezing point of a pure solvent, more molecules of the solvent pass from solid to liquid phase i.e., solid solvent begins to melt when a solute is added to it.

Solution (solvent+solute) $\rightleftharpoons$ Solvent (solid). Consequently to prevent the melting of the solid, the temperature is to be lowered than the actual freezing point of the pure solvent. At this lower temperature freezing occurs and a new equilibrium is established in the system. It has been observed that the lowering of freezing point of a solvent is directly proportional to the number of moles of the solute present in a particular amount of solvent.

$$\Delta T_f \propto m$$

or, $\Delta T_f = K_f.m. \ldots (1)$

Where, ΔT_f = depression of the freezing point

m = number of moles of a solute present in 1 kg (1000 g) of solvent.

K_f = constant, called molal freezing point depression constant or cryoscopic constant of the solvent.

The equation (1) may be expressed as—

$$\Delta T_f = \frac{1000 \times K_f \times w}{M \times W}$$

$$\text{or, } M = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Where w is the weight of solute and W is the weight of solvent and M is the molecular weight of the solute.

Sometimes the value of the K_f is given per 0·1 kg (100 g). In such case the expression becomes—

$$M = \frac{100 \times K_f \times w}{\Delta T_f \times W}$$

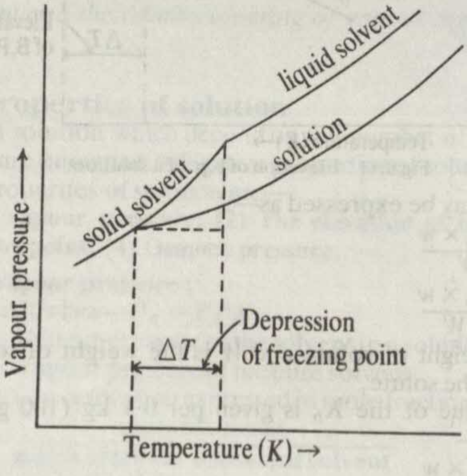


Fig 8.12 : Depression of F.P. of a solution.

(4) Osmotic pressure :

When a solution of a non volatile solute is separated from the solvent by a semi-permeable membrance, it is observed that the membrance permits the solvent molecules to pass through its pores but the solid molecules are not allowed to pass through the pores. As a result the solvent molecules diffuse from one side to the other through the membrance. As the vapour pressure of the solution side is less than that of the solvent side, more solvent molecules pass from the solvent side through the membrance to the solution side. As a result the liquid level on the solution side rises up. This phenomenon which results in a net flow of the solvent to the solution is known as osmosis.

- ***Thus osmosis is the diffusion of solvent through a semipermeable membrane from a solvent into a solution or from a dilute solution into a more concentrated solution.***

A time comes when the level of the solution and solvent side becomes stationary. At this stage an extra pressure of height '*h*' of the liquid column acts on the solution side. Thus the extra pressure produced on the solution side due to osmosis is known as osmotic pressure. Osmotic pressure being a colligative property of solution is similarly proportional to lowering of vapour pressure. It is represented as π (Pi). It can be expressed as—

$$\pi = \rho g h$$

where ρ = density of the solution.
h = difference of liquid levels in the two sides of the membrance.
g = acceleration due to gravity.

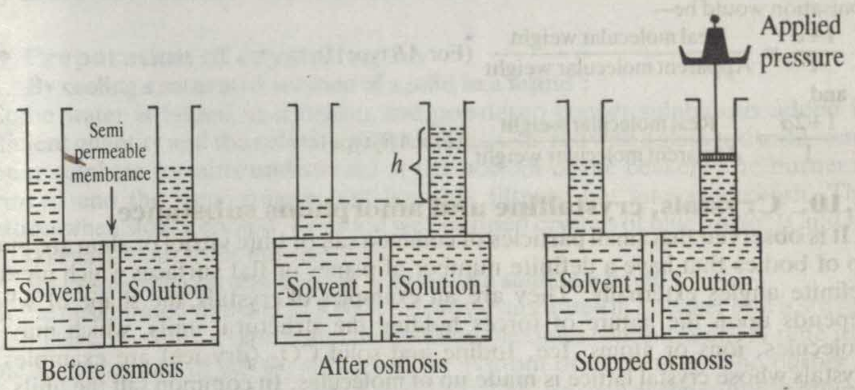


Fig 8.13.

The net flow of the solvent into the solution can be stopped by applying extra pressure π on the solution side.

Osmotic pressure and the amount of solute.

The osmotic pressure is directly proportional to the quantity of the solute present in a given volume of soln. The relation between the osmotic pressure and the moles of solute is given by the equation—

$\pi \propto n_B$ T/V or $\pi = n_B$ RT/V ; R = (gas constant).

where, π = osmotic pressure, n_B = moles of solute, V = Volume of solution, T = temperature in Kelvin scale.

Osmotic pressure and molarity :

Since n_B/V = molarity = C, We get $\pi = CRT$.

- **Osmotic pressure, association and ionisation of solute :**

Just like other colligative properties, osmotic pressure is also affected by association and dissociation of the solute. Association of the solute lowers the osmotic pressure but ionisation or dissociation of solute will exibit higher magnitude of osmotic pressure than its unionised state.

If α be the degree of association or dissociation for a molecule AB, then—

$$\frac{1}{1+\alpha} = \frac{\text{Expected osmotic pressure if not ionised}}{\text{Actual osmotic pressure after association or ionisation}}$$

Similarly for a solute AB_2

$$\begin{array}{llll} & AB_2 & \rightleftharpoons A^{++} & + 2B^- \\ \text{Before ionisation} & 1 & 0 & 0 \\ \text{After ionisation} & (1-\alpha) & \alpha & 2\alpha \end{array}$$

Hence in such case—

$$\frac{1}{1+2\alpha}=\frac{\text{Expected osmotic pressure if not ionised}}{\text{Actual osmotic pressure after association or ionisation}}$$

The above formula can be applied to other three colligative properties. For molecule AB type—

$$\frac{1}{1+\alpha}=\frac{\text{Expected colligative property}}{\text{Actual colligative property}}$$

Again for molecule AB_2 type—

$$\frac{1}{1+2\alpha}=\frac{\text{Expected colligative property}}{\text{Actual colligative property}}$$

The corresponding relationship between molecular weight of the solute and the degree of ionisation would be—

$$\frac{1+\alpha}{1}=\frac{\text{Real molecular weight}}{\text{Apparent molecular weight}}\ \text{(For } AB \text{ type)}$$

and

$$\frac{1+2\alpha}{1}=\frac{\text{Real molecular weight}}{\text{Apparent molecular weight}}\ \text{(For } AB_2 \text{ type)}$$

8.10. Crystals, crystalline and amorphous substance.

It is observed that small particles of common salt or blue vitriol or alum are made up of bodies that have a definite number of planes or flat surfaces which meet at definite angles externally. They are all examples of crystals, the shape of which depends upon the nature of forces holding the structural units, which may be molecules, ions or atoms. Ice, Iodine and solid CO_2 (dry ice) are examples of crystals whose crystal lattice is made up of molecules. In common salt the units are Na^+ and Cl^-, while in metals the structural unit is metallic atom. Crystals are formed by careful and slow cooling of a saturated solution of the concerned salt. On the other hand when some liquids are allowed to cool they do not from crystalline shape. Their internal structure is not rigid, the structural units being in haphazard manner. They are in fact shapeless. This type of solids are called amorphous solids. *Glass* is a classic example of amorphous solid. Other example being *lime, pitch* etc.

- *A crystal may be defined as a homogeneous solid with a regular polyhedral shape which is bounded by plane faces that meet in sharp edges. All crystals of the same substance grow so that they have the same angles between their faces. Since different faces can grow at different rates depending upon the conditions of crystallisation, the crystals may not have the same external appearance.*

Every crystal has its own crystalline form which is acquired during its formation from saturated solution. Some are *prismatic*, other may be *pyramidal, cubical, octahedral, tetrahedral* etc. 280 different types of crystalline structures are known. It should be noted that crystalline shape is not the only criteria of crystal. Solid glass can be cut into fine crystalline geometrical shape, yet glass is not crystal, it is amorphous. On the other hand if we break a crystal of blue vitriol, the smaller minute particles will also have the same crystalline shape.

- **Crystallisation :**

Crystallisation is a process of formation of fine crystals by cooling or evaporating a saturated solution of a solute in a solvent.

The solvent left after the separation of a crystal is called **Mother liquor.**

Sometimes it is observed that during crystallisation from a saturated solution, same solid with two or more different crystalline forms are being separated out. Both elements and compounds exhibits this property. In the case of compounds, this phenomenon is known as *polymorphism* and in the case of element it is called *allotropy*. The terms *dimorphism, trimorphism* etc., are given to the substances having two, three or more different crystalline forms. Crystalline carbon exists in two allotropic forms —Diamond and Graphite. Compounds like SiO_2, HgI_2 exist in different crystalline forms. Again two or more different compounds crystallise in the same crystalline structure. The phenomenon is called *Isomorphism* e.g., $KClO_4$ and $KMnO_4$; $ZnSO_4$, $7H_2O$ and $FeSO_4$, $7H_2O$ etc. *Isopolymorphism* is a phenomenon in which each of the two or more forms of a polymorphic substance is isomorphous with a form of another polymorphic substance e.g., As_2O_3 and Sb_2O_3 are isodimorphous. SnO_2 and TiO_2 are isotrimorphous. Bivalent sulphates of molecular formula MSO_4, $7H_2O$ where M=Mg, Zn, Ni, Mn and Co are iso-dimorphous since they exist in both rhombic and monoclinic form.

• Preparation of crystal :

1. **By cooling a saturated solution of a solid in a liquid :**

Some water is boiled in a beaker and powdered copper sulphate is added in sufficient quantity and the solution is continuously stirred with a glass rod until some copper sulphate remains undissolved at the bottom of the beaker. The burner is removed and the clear supernatant liquid is filtered hot into a petridish. The solution when slowly cooled, beautiful well defined crystals of blue vitriol ($CuSO_4$, $5H_2O$) separate out from the solution.

2. **By evaporating an unsaturated solution of a solid in a liquid :**

Some unsaturated solution of KNO_3 is slowly evaporated in a beaker and is stirred with a glass rod. With evaporation the solution becomes concentrated. A time will come when crystals of KNO_3 appears at the bottom of the beaker. The burner is immediately removed. The beaker is slowly cooled. As soon as the solution attains room temperature solid crystalline KNO_3 will be separated from the solution. Slow cooling forms well defined large crystals while rapid cooling forms small crystals.

3. **Formation of overgrowth :**

A saturated solution of potash alum [K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$] is taken in a beaker. Now a small crystal of potash alum is allowed to hang into the solution with the help of a string. It will be observed that the size of the suspended potash alum crystal gradually increases. This is due to the deposition of potash alum crystal from the solution on the surface of the suspended crystal.

4. **By solidifying molten substance :**

Some small pieces of sulphur is melted in a porcelain basin. It is now allowed to cool. A solid crust is formed on the surface. The crust is pierced through a glass rod and the liquid molten sulphur is thrown out. Large needle shaped crystals of prismatic sulphur are found to be formed on the surface of the basin.

5. **By sublimation :**

Substances like *Iodine, Sal ammoniac* etc., can be crystallised by subliming the solid and cooling the vapour.

8.11. Uses of crystallisation.

(I) Re-crystallisation :

If some solid substance contains some soluble impurites, then it is dissolved in minimum volume of chosen solvent and then warmed to concentrate the solution. The pure substance will be separated out on slow cooling of the solution. The impuritis remain in the mother liquor. This is called *re-crystallisation*. The process is frequently used in organic synthesis.

(II) Fractional crystallisation :

If several solid solutes of different solubilities be dissolved in a solvent then on concentrating the solution after evaporation followed by slow cooling, the least soluble substance crystalises out first, leaving the other solutes in the mother liquor. This phenomenon is called fractional crystallisation. Thus *fractional crystallisation consists in the separation of mixtures of solid solutes having different solubilities from a solution containing them, by evaporation and crystallisation through slow cooling.*

Both sodium chloride and potassium nitrate are soluble in water but the solubility of KNO_3 is more than that of NaCl. Therefore, both NaCl and KNO_3 can be obtained in pure state by the process of fractional crystallisation from an aqueous solution containing both of them. The aqueous solution containing them when evaporated and slowly cooled, NaCl being less soluble than KNO_3 will be crystallised out first. This is filtered and the filtrate on further cooling yields KNO_3.

Experiment : An aqueous solution containing sodium nitrate and copper sulphate is taken on a porcelain basin. The solution is concentrated by evaporation (Fig 8.14). The solution is now slowly cooled. Copper sulphate being less soluble than sodium nitrate will crystallise out first. The separated crystals are filtered off washed with little water. Than crystals are then dissolved in minimum volume of water and recrystallised. Deep blue coloured crystals of blue vitriol $CuSO_4, 5H_2O$ separate out. The solution left after the separation of blue vitriol is further evaporated and cooled when colourless crystals of $NaNO_3$ are separated out. The separated crystals are filtered off and dissolved in minimum volume of water and recrystallised, when pure $NaNO_3$ crystals are obtained.

Fig. 8.14.

8.12. Water of crystallisation.

Crystals of copper sulphate is deep blue in colour. On heating a few crystals of copper sulphate, the following changes occur :

(i) water vapour escapes from the crystals and is deposited on the upper cooler part of the test tube,

(ii) the crystals crumble to fine powder and

(iii) the colour changes to white.

$$\underset{\text{Deep blue crystals}}{CuSO_4, 5H_2O} \xrightarrow{100°C} \underset{\text{Pale blue powder}}{CuSO_4, H_2O} \xrightarrow{250°C} \underset{\text{White powder}}{CuSO_4}$$

On the basis of the above experiment, water of crystallisation may be defined as follows :—

Water present in crystalline compounds in definite proportions acquired during crystallisation of a solid from a saturated solution is known as water of crystallisation. The substance is called hydrated crystal or simply hydrate. The number of water molecule present in the hydrate is fixed. The colour and structure of the hydrate is governed by the number of molecules of water of crystallisation.

Examples : Blue vitriol [$CuSO_4, 5H_2O$], Borax [$Na_2B_4O_7, 10H_2O$] ; Glauber's salt, [$Na_2SO_4, 10H_2O$], oxalic acid [$H_2C_2O_4, 2H_2O$] etc. Water is an essential part of the constitution of the hydrate, but a large number of well-defined crystals are known, which do not contain any water of crystallisation. They are called *anhydrous salts.* e.g., NaCl, KNO_3, KCl, NH_4Cl, K_2SO_4 etc. On heating a hydrate, water of crystallisation is escaped and the solid crumbles to powder. There are some hydrates which on heating do not form anhydrous salts. On the contrary they are hydrolysed by their own water of crystallisation to form metal oxides.

$$MgCl_2, 6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O$$
$$2[AlCl_3, 6H_2O] \xrightarrow{\Delta} Al_2O_3 + 6HCl + 9H_2O$$

[Water present in the crystals is held in various ways. They may occupy Lattice position in the crystals or they may form bonds with cations or anions. The structure of copper sulphate is worth noting. In copper sulphate molecule ($CuSO_4$, $5H_2O$) each Cu^{++} ion is co-ordinated to four water molecules through the lone pairs on the oxygen atom to form the copper $[Cu(H_2O)_4]^{++}$. Each sulphate ion has one water molecule held by hydrogen bonding and is very firmly held. This explains why blue vitriol loses 4 comparatively weakly bound water molecules at 100°C but only at 250°C the fifth water molecule is lost to form anhydrous salt (Fig. 8·18).

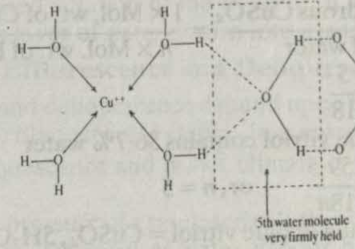


Fig. 8.15.

8.13. Determination of water of crystallisation of blue vitriol :

Principle : Whenever a hydrate of known weight is heated, it forms anhydrous salt. During heating care should be taken so that the hydrate loses water completely and the salt does not undergo any chemical reaction. The weight of the anhydrous salt is determined and the difference between the hydrate and the anhydrous salt will give the weight of water which the hydrate contains.

Method : A pair of clock glasses held together by a clip is taken and weighed in a chemical balance. Some blue vitriol is taken on one of the clock glass, covered with the other and the whole is weighed again. The difference gives the weight of blue vitriol. The upper clock glass is slided to escape steam and the apparatus is now placed on an air oven and is heated by bunsen flame carefully first to 100°C and then to 230°C. Heating is continued for about 1 hour. The salt becomes anhydrous and white. It is cooled in a desiccator and is weighed. The processes of heating, cooling and weighing are continued till the final weight is constant.

Calculation :

Let the weight of the pair of clock glass with clip $= w$ g
Let the weight of the pair of clock glass with crystal $= w_1$ g
Weight of the hydrated salt $= (w_1 - w)$ g
Again weight of the pair of clock glass with clip + dehydrated salt $= w_2$ g
Weight of the dehydrated salt $= (w_2 - w)$ g
Weight of water of crystallisation $= (w_1 - w) - (w_2 - w)\text{ g} = (w_1 - w_2)$ g

Now,

$(w_1 - w)$ g of the hydrated salt contains $(w_1 - w_2)$ g of water of crystallisation

$\therefore$ 100 ,, ,, ,, ,, ,, ,, $\dfrac{(w_1 - w_2)\times 100}{w_1 - w}$ g of water of crystallisation.

The air oven must be fitted with a thermometer to record the temperature of dehydration. This is very important otherwise the compound may suffer complete chemical decomposition. The temperature of dehydration must be known before the experiment.

- **Deduction of the formula of the blue vitriol :**

The number of water molecules, hence the molecular formula of the hydrate may be easily deduced, once the amount of water present in the hydrate is known.

Let the molecular formula of blue vitriol be $CuSO_4, nH_2O$.

Where n = number of water molecule present in blue vitriol.

Anhydrous $CuSO_4 : H_2O = 1 : n$

In the experiment it is mentioned that the weight of anhydrous $CuSO_4 = (w_2 - w)$ g

Weight of water of crystallisation $= (w_1 - w_2)$ g

Molecular weight of anhydrous copper sulphate = 159·5.

$$\therefore \frac{\text{Weight of anhydrous } CuSO_4}{\text{Weight of water}} = \frac{1 \times \text{Mol. wt. of } CuSO_4}{n \times \text{Mol. wt. of } H_2O}$$

$$\text{Or, } \frac{w_2 - w}{w_1 - w_2} = \frac{159{\cdot}5}{n \times 18}$$

Experiment shows that Blue vitriol contains 36·7% water

$$\therefore \frac{100 - 36{\cdot}07}{36{\cdot}07} = \frac{159{\cdot}5}{18n} \quad \text{or, } n = 5$$

$\therefore$ Molecular formula of blue vitriol $= CuSO_4, 5H_2O$.

8.14. Efflorescence and Efflorescent substance.

Some crystalline solids containing water of crystallisation on exposure to air at ordinary temperature loses water of crystallisation fully or partially. As a result, the crystals crumble to fine powder. The hydrated salts which display this peculiar property are called efflorescent substances and the phenomenon is called efflorescence.

- *Efflorescence is the phenomenon in which a crystalline hydrate, on exposure to air at ordinary temperature, loses its water of crystallisation partly or wholly forming a powdery deposit on the crystals.*

Example : $Na_2CO_3{\cdot}10H_2O$ is an efflorescent solid. If this crystal is kept in atmosphere, it loses 9 molecules of water of crystallisation (per molecule) to the air forming Na_2CO_3, H_2O. The crystal loses its geometrical shape and weight.

$$Na_2CO_3, 10H_2O \longrightarrow Na_2CO_3, H_2O + 9H_2O\uparrow$$

Glauber's salt ($Na_2SO_4, 10H_2O$) is another efflorescent solid. On exposure to air it loses whole of its water of crystallisation. The process is a spontaneous one at room temperature.

Cause :

A hydrate displays efflorescence and is converted into a lower hydrate or anhydrous salt if the water vapour pressure of the atmosphere is lower than the equilibrium water vapour pressure of the hydrate. As a result of this, water of the crystals escapes to the almosphere in the form of vapour. Thus a hydrate which does not effloresce in Assam where the air is moist, may do so in the desert areas of Rajasthan having dry air.

8.15. Deliquescence and Deliquescent substance.

There are some substances which when exposed to air at room temperature absorb moisture, become moist and finally dissolve in the absorbed moisture. In extreme case a concentrated solution of the salt is formed.

- *Deliquescence is the property of absorption of moisture from the atmosphere by a hygroscopic solid to such an extent that a concentrated solution of the solid may* *eventually be formed. The substance which possesses such property is called a deliquescent substance.*

Examples : Hydrated salts like $CaCl_2$, $FeCl_3$, $MgCl_2$, $Fe(NO_3)_3$ etc., are good examples of deliquescent substances. During rainy season they become liquid unless they are kept in air tight container. Pure sodium chloride is not a deliquescent substance, yet in the rainy season common salt becomes "liquid". This is because of the fact that common salt contains $CaCl_2$, $MgCl_2$ asimpuritieswhich are hygroscopic, deliquescent substances. In the absorbed moisture from air especially in the rainy season, NaCl becomes liquid. However, pure NaCl i.e., table salt does not wet in the rainy season.

Cause : If the atmospheric water vapour pressure is higher than the water vapour pressure of the saturated solution of the hydrate, it will show deliquescence and becomes coated with a layer of water or turn into a saturated solution.

- **Temperature, Efflorescence and Deliquescence :**

Both efflorescence and deliquescence depend upon the temperature. Thus at low temperature say 20°C, blue vitriol is stable. In a more humid atmosphere $CuSO_4, 5H_2O$ may show deliquescence and in hot climate it may effloresce. This can be explained as follows:

At 50°C, the vapour pressure of a saturated solution of $CuSO_4$ in equilibrium with water vapour is 90 mm. Removal of water vapour by a pump will result in the crystallisation of $CuSO_4, 5H_2O$. When all the water is removed from the liquid phase the solid phase of $CuSO_4, 5H_2O$ will be in equilibrium with water vapour. The vapour pressure at this stage at 50°C is 47 mm. If water is further lost, lower hydrates will be formed with the decrease of vapour pressure. This is shown in the table (Temp. 50°C).

Substance	Vapour Pressure
Saturated solution of $CuSO_4$	90 mm
$CuSO_4, 5H_2O$ (solid)	47 mm
$CuSO_4, 3H_2O$ (,,)	30 mm
$CuSO_4, H_2O$ (,,)	4·5 mm

Hence solid $CuSO_4, 5H_2O$ will display efflorescence at 50°C when the water vapour pressure in the atmosphere is below 47 mm. If the external vapour pressure is more than 90 mm at 50°C, $CuSO_4, 5H_2O$ will absorb more moisture from the atmosphere i.e., it will deliquesce. If the water vapour pressure is between 47 and 90 mm then at 50°C, $CuSO_4, 5H_2O$ will remain stable, neither display efflorescence nor deliquescence. At 20°C the vapour pressure of $CuSO_4, 5H_2O$ is about 5 mm and that of a saturated solution of $CuSO_4$ is 16 mm. Therefore $CuSO_4, 5H_2O$ will be stable at 20°C if the water vapour pressure lies between 5 and 16 mm. This explains why in cold countries $CuSO_4, 5H_2O$ is neither efflorescent nor deliquescent. The following table predicts the stability of some hydrates at 20°C with an atmospheric vapour pressure = 14 mm.

Solid	Vapour pressure of the hydrate	Vapour pressure of saturated solution	Prediction of stability
1. $CuSO_4, 5H_2O$	5 mm	16 mm	Stable
2. $CaCl_2, 6H_2O$	2·5 ,,	7·5 ,,	Deliquescent
3. $Na_2SO_4, 10H_2O$	16·3 ,,	16·6 ,,	Efflorescent
4. $Na_2CO_3, 10H_2O$	24·2 ,,	26·0 ,,	Efflorescent

• Hygroscopic substance :

There are some substances which spontaneously absorb moisture from the atmosphere when exposed in air or kept in contact with some wet substance but do not dissolve in the absorbed moisture unlike deliquescent substances. These are called hygroscopic substances e.g., Silica gel, conc. H_2SO_4, quick lime, anhydrous copper sulphate etc.

• Colloids •

The foundation of colloid was laid by *Thomas Graham* (1861). In course of his investigation on diffusion of solution through parchment paper Graham observed that some substances in solution readily diffused through the parchment paper while others diffused with exceedingly slow rate. Graham called the former class of substances *Crystalloids* and the other class of substances that does not pass through the parchment paper readily, were called by him *colloids*. The former class includes solids like *common salt, sugar, urea* etc. and the later group includes starch, gelatine, glue etc. According to Graham colloids constitute a separate kind of matter like solid, liquid and gaseous state. But this idea of 'colloid being a separate class of substance', was proved to be wrong. It is now known, that colloid is not a particular class of substance. By applying suitable method crystalloid substance can be prepared in such a way that like colloids they would not diffuse through the parchment paper. In fact, *the same substance may act as colloid in one medium and crystalloid in other medium.* For example, NaCl acts as a crystalloid in its aqueous solution but it forms colloidal suspension in benzene. Soap acts as colloid in aqueous solution but act as crystalloid in alcohol. It follows therefore, a division of substances into crystalloids and colloids is an impossible task. The term colloid is now applied *to a particular state of matter*—hence the term *colloidal state is now used instead of colloidal substance.*

8.16. Suspension, colloidal state and true solution.

A system which is made up of a substance distributed in very fine particles through another substance is called *dispersion system* and the substance which is distributed is known as the *dispersed phase.* The continuous medium around the distributed substance in known as *dispersion medium* or external phase. Depending on the degree of dispersion, the dispersion system is divided as *true solution, colloid* and *suspension.*

(1) **Suspension** : Fine particles of insoluble substances like sand, chalk etc., when added to water and the mixture is stirred, it becomes turbid, The fine particles move about freely in water. If this turbid mixture is left for some time without any disturbance, the retatively heavy particles settle down due to the gravitational force but the more fine particles remain suspended in water. The diameter of these fine particles is more than 10^{-4} cm. This mixture of the fine particles in water is called *suspension.* Partial settlement of these particles takes place if it is kept for a long period of time. The particles are large enough to be seen by eye with or without the aid of microscope.

(2) **True solution** : When sugar is dissolved in water, the sugar molecules dissociate and enter into the intermolecular space of water and form a homogeneous solution. Neither the solute particles nor the solvent one is observed by human eye or with the aid of microscope. The diameter of sugar particles is less than or equals to 10^{-8} cm. The resulting mixture is called true solution. Such solution can easily pass through filter paper and also through the parchment paper. Hence the true solution is defined as *the solution containing solute particles of diameter equals to or less than 10^{-8} cm distributed uniformly throughout the entire mass of the solvent.* As a mattter of fact, a true solution is a solution of crystalloid in a solvent. It contains molecules or ions. A true solution is electrically neutral.

(3) **Colloids** : In between the above two states of matter, there is a separate state, in which the diameter of the particles ranges from 10^{-5} cm to 10^{-7} cm. The colloid particles are too small to be seen by ordinary microscope—they can only be

observed by ultra microscope. Thus a mixture of barly or glue in water never settles down but forms heterogeneous stable suspension. These particles are colloids.

- *When particles of diameter 10^{-5} cm to 10^{-7} cm of an insoluble substance are kept in suspension in solvent where they move freely, do not form a clear solution but form a translucent heterogeneous mixture from which the particles can not be removed by passing through parchment paper, are called colloids.*

Thus it can be concluded that nature of the solution is governed by the size of the particles of solute.

(a) The particles become insoluble and form suspension when the diameter of the particles is more than 10^{-4} cm.

(b) A colloid results, if the diameter of the particles ranges from 10^{-7} cm to 10^{-5} cm.

(c) A true solution contains particles, the diameter of which is less than 10^{-8} cm.

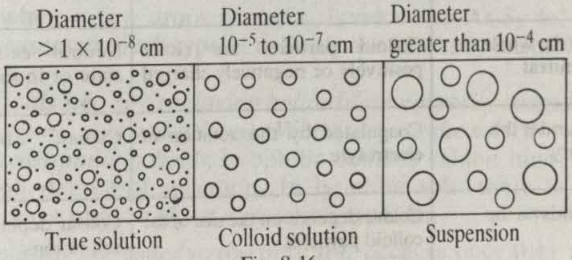

Diameter $> 1 \times 10^{-8}$ cm
Diameter 10^{-5} to 10^{-7} cm
Diameter greater than 10^{-4} cm
True solution
Colloid solution
Suspension

Fig. 8.16.

- **Definition :** *A colloid is a two phase heterogeneous system in which the medium constitutes one phase and the dispersed substance another phase. The medium is known as dispersion medium and the substance which remains dispersed is the disperse phase. The disperse phase has diameter between 10^{-7} to 10^{-5} cm.*

The colloid particles and the medium in which the particles are dispersed constitute colloidal system. The fine particles may be solid, liquid or gas and the disperse medium may also be solid, liquid or gas.

The table below gives the examples of various colloidal system.

Disperse phase	**Dispersion medium**	**Examples**
(1) solid	gas	Smoke and dust, consisting of solid particles suspended in air **(Solid aerosol)**
(2) solid	liquid	Finely divided metals suspended in liquids e.g., gold sol, curd, jelly.
(3) solid	solid	Finely divided gold in ruby glass
(4) liquid	gas	Clouds, fog, mists—these consists of water droplets in air *(aerosol)*
(5) liquid	liquid	Emulsion e.g. Milk
(6) liquid	solid	Butter, cheese
(7) gas	liquid	Foams, Froths
(8) gas	solid	Foam rubber, pumice stone

- **Difference between suspension, colloids and true solution.**

Suspension	Colloids	True solution
(1) Diameter of the particle is equal to or more than 10^{-4} cm. Diameter >1000 Å	Diameter of particle is in between 10^{-5} to 10^{-7} cm. Diameter (10Å—1000Å)	Diameter of the particle is less than 10^{-8} cm. Diameter <10Å
(2) Particles are visible by naked eye or by microscope.	Particles are not visible by naked eye or by microscope—but can be observed by ultra microscope.	Not visible even by ultra microscope
(3) Heterogeneous,—two phase system	Heterogeneous,—two phase system	Homogeneous—one phase system
(4) Particles and the whole system are neutral	Colloid particles are either positively or negatively charged	Neutral—exists either in ionic state or in the molecular form
(5) Precipitates under the force of gravity	Coagulated by the addition of electrolyte	Cannot be coagulated
(6) Colour depends on the particles	Colour depends on the size of the colloid particles	Colour depends on the soluble salt or ions
(7) Light can not pass.	Exhibits tyndal effect	Does not exhibit tyndal effect
(8) Can not pass through filter paper or parchment paper	May pass through filter paper but can not pass through parchment paper	Can easily pass through filter paper or parchment paper
(9) Undergoes electrolysis	Undergoes cataphoresis	Undergoes electrolysis
(10) Can not pass through a dialyser	Can not pass through a dialyser	Can pass through dialyser
(11) Brownian movement may occur	Exhibits Brownian movements	The particles do not exhibit Brownian movements

- **Classification of colloids :**

Colloids can be classified into various groups in accordance with specific properties. Some classifications are given below :

(1) Sols and Gels :

Depending upon the viscosity, colloids are classified as *sols* and *gels*. Low viscose type is called *Sol* while colloid with higher viscosity is called *Gel* . Thus a starch solution in water at higher temperature is a fluid having low viscosity and can flow easily while at low temperature the same colloid becomes more viscose and does not flow and is about to set. The former is an example of sol while the latter is gel. The transformation of gel into sol is usually brought about by applying mechanical force or raising temperature.

(2) **Suspension and emulsion :**

Colloids are also classified as suspension and emulsion. Suspension refers to a colloid where the dispersed phase is a solid which is dispersed in a liquid, on the other hand in emulsion a liquid is dispersed in another liquid medium. A suspension may be lyophobic and lyophilic but emulsions are in most cases lyophilic. When a mixture of oil and water is vigorously stirred with a glass rod in presence of soap, emulsion results.

[3] **Lyophobic and lyophilic colloids :**

Depending upon the nature of disperse phase and despersion medium, the colloidal suspension in liquid media is classified as **lyophobic** and **lyophilic** colloids.

Lyophobic i.e., solvent hating colloids have a natural tendency to come out of the medium. When water is the solvent, such type of colloids are known as hydrophobic colloids. e.g., when a few drops of $AlCl_3$ is added to As_2S_3 sol in water, it is immediately coagulated. Such type of colloids are generally unstable and sensitive to electrolytes.

Lyophilic colloids i.e., solvent loving colloids are not easily coagulated by adding electrolyte, e.g., gum, glue and gelatine. When water is the solvent such colloids are referred to as hydrophilic colloids. Lyophilic colloids exhibit high affinity for the solvent i.e., high degree of solvation. In lyophilic sols, there is an interaction between the disperse phase and the dispersion medium.

Lyophobic colloids are called irriversible sol, because once they are coagulated from the medium they can not be reconverted into sol by mixing again. *Lyophilic colloids are reversible* because if the disperse phase is separated from the medium, they can be reconverted simply by mixing.

• Difference between lyophobic and Lyophilic sols.

Lyophobic sols	Lyophilic sols
(1) Each colloid particle consists of atoms or molecules e.g., sulphur, sulphides, halides of Ag.	(1) Each colloidally dissolved unit in liquid is a single macro-molecule, e.g., gum, starch, soap etc.
(2) Surface tension is similar to that of dispersion medium.	(2) Surface tension is often lower than that of dispersion medium.
(3) Viscosity does not differ much from that of the medium.	(3) Viscosity is much higher than that of the medium.
(4) Lyophobic colloids are irriversible.	(4) Lyophilic colloids are reversible.
(5) Less stable, as they are stabilised mainly by the charge present on the surface of the colloid particles.	(5) Thermo dynamically more stable as they are stabilised by the force of solvation.
(6) The particles are visible with the aid of ultra microscope.	(6) Not detectable by an ultra microscope.
(7) Precipitation (coagulation) is caused by the addition of a small amount of electrolytes.	(7) Dispersed particles are not precipitated by small amount of electrolytes. Large amount of electrolyte causes salting out.

Lyophobic sols	Lyophilic sols
(8) Particles migrate in one direction in an electric field depending upon the charge they bear.	(8) The particles may migrate in either direction or may not miagrate in an electric field depending upon the pH of the medium.
(9) Colligative properties are insignificantly small.	(9) Colligative properties are well marked.
(10) Physical properties follow the law of mixture.	(10) Physical properties do not follow the law of mixture.

• Preparation of colloids.

(i) *Lyophilic colloids* like glue, gelatine, gum, starch etc., can be prepared by dissolving them in finely divided state in suitable solvent (water) in hot, followed by cooling at room temperature. Dispersed phase can be recovered by evaporating the dispersing medium (water).

(ii) *Lyophobic colloids* cannot be obtained by the above-mentioned method as they have least affinity towards the solvent. Special methods have been developed in which the size of the particles is to be increased or decreased. These methods are of two types.

[A] **Dispersion methods :** In this method the size of the particles is reduced.

[B] **Condensation method :** In this method the size of the particles is increased.

[A] Dispersion method : In this method the coarser particles are reduced to the dimension of the colloid particles by some appropriate mechanical means.

(i) **Mechanical dispersion :** The substance to be dispersed is ground to fine state followed by dispersions in a medium to form coarse suspension. It is then placed in a colloid mill which contains a series of round metallic discs each rotating at a high speed in opposite directions. This movement of the discs reduces the coarse particles into the colloidal size. A protective agent is added before the grinding in colloid mill. The agent stabilizes the sol and prevents from coagulating.

(ii) **Bredig's arc method :** This method is used in the preparation of colloidal sol of metals like Ag, Au, Pt etc. Two electrodes of metals to be dispersed are dipped in a vessel containing cold water mixed with KOH which acts as stabiliser. The vessel is kept cool by placing it in a freezing mixture. Electric arc at high voltage is struck between the electrodes. The heat of the arc at first vaporises the metals and

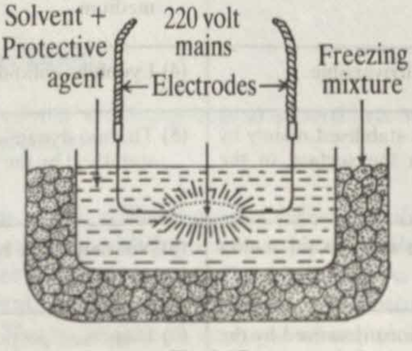


Fig. 8.17

the colloidal particles of desired dimensions are formed subsequently due to condensation.

(iii) **Peptization :** Peptization is a process of conversion of a precipitate into colloidal sol by adding a suitable electrolyte. Thus when freshly precipitated $Fe(OH)_3$ is treated with a trace of $FeCl_3$, the resulting mixture is peptized i.e., forms colloidal sol. Here $FeCl_3$ acts as a peptizing agent. The peptizing action is due to the adsorption of one of the common ion of the electrolyte i.e., the peptizing agent. The electrically charged particles then split off the precipitate to form colloidal particles. Colloidal NiS, or CdS can be obtained by passing H_2S through the precipitates of NiS and CdS in warm water.

[B] Condensation method : This method consists in condensing the particles in true solution present as ions or molecules, into colloidal size by chemical reaction. The method may involve reduction, oxidation, double decomposition, hydrolysis, exchange of solvent etc.

(i) **Reduction :** In this method the reducing agents are H_2, PH_3, CO, HCHO, N_2H_4, $C_6H_5NH\,NH_2$ etc. A silver sol is obtained by passing H_2 through a suspension of Ag_2O in water at 50°C. Colloidal gold is obtained by reducing $AuCl_3$ with HCHO.

(ii) **Oxidation :** When H_2S is passed through bromine water at room temperature H_2S is oxidised to give sulphur sol.

$$Br_2 + H_2S = 2HBr + \underset{\text{(sol)}}{S\downarrow}$$

(iii) **Double decomposition :** As_2S_3 sol is obtained by the action of H_2S on a solution of As_2O_3. Excess of H_2S is removed by boiling.

$$As_2O_3 + 3H_2S = \underset{\text{(sol)}}{As_2S_3} + 3H_2O$$

(iv) **Hydrolysis :** This method is extensively used for the preparation of sols of oxides and hydroxides of metals like Fe, Al and some non metals. $FeCl_3$ when hydrolysed with water yields ferric hydroxide sol.

$$FeCl_3 + 3H_2O = \underset{\text{(sol)}}{Fe(OH)_3} + 3HCl$$

Silicic acid sol is obtained by adding HCl to sodium silicate till the mixture is acidic. The mixture is purified by dialysis. Colloidal silicic acid is also obtained by the hydrolysis of $SiCl_4$.

$$SiCl_4 + 4H_2O = \underset{\text{(sol)}}{H_4SiO_4} + 4HCl$$

(v) **By exchange of solvent :** Addition of alcoholic solution of resin to excess water results in the formation of colloidal resin. Sols of gum mastic, sulphur, phosphorus etc., can be prepared by pouring their alcoholic solution to excess amount of water.

(vi) **Emulsification :** An emulsion is obtained when a mixture of oil and water is vigorously stirred with soap (sodium oleate).

• Purification of colloids :

Sols prepared by the above methods are contaminated with some electrolyte, which may be removed either by dialysis or by ultrafiltration process.

(i) **Dialysis :** *The method of separation of a crystalloid from a colloid by passing the mixture of the two, through a membrane of parchment paper, or fish bladder or collodion membrane, is known as dialysis.*

Colloidal particles can pass through a filter paper but cannot pass through parchment paper, fish bladder or collodion membrane through which however ion or crystalloid can pass easily. Separation of colloid from a crystalloid is based upon this observation.

Experiment : The apparatus used for the separation of a colloid from a crystalloid is known as *dialyser*. The open end of the base of a bell jar is closed with a parchment paper. A mixture of a solution of KI (crystalloid) and starch solution (colloid) is kept inside the jar which is then suspended from a rod and partially immersed in water in a large vessel. After sometime few drops of Cl_2 water is added to the water on the outer vessel and the water becomes brown. $2KI + Cl_2 = 2KCl + I_2$. This proves that only KI (crystalloid) has passed through the parchment paper from the bell jar to the water of the outer vessel but not the starch solution. If both of them were passed through parchment paper simultaneously, then the addition of Cl_2 water would turn the whole solution blue.

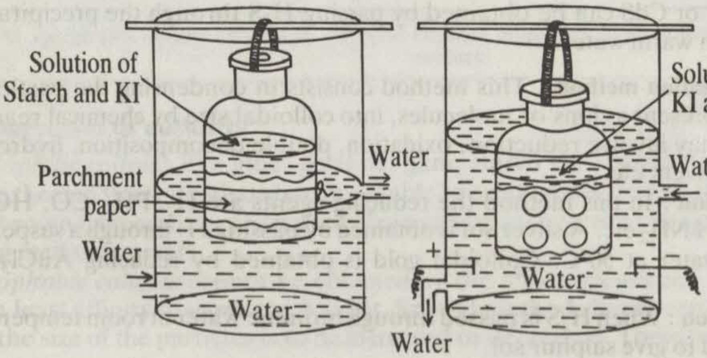


Fig. 8.18

$$2KI + Cl_2 = 2KCl + I_2$$
$$I_2 + \text{starch soln.} \rightarrow \text{blue colour.}$$

If the process is continued, the whole of KI (crystalloid) will come out leaving behind the starch solution (colloid) into the bell jar. The water of the outer vessel must continuously be changed, otherwise if equilibrium is reached between the solution inside the bell jar and the water outside, KI solution (crystalloid) would not come out of the bell jar. If hot water is used in the outer vessel instead of cold water, the diffusion of crystalloid takes place at much quicker rate (hot dialysis).

(ii) **Electro-dialysis :** The rate of dialysis is much increased by carrying out the dialysis in an electric field. This process is known as electro-dialysis. This process is applicable only when the crystalloids are electrolytes. If the impurities present in a colloid are non electrolytes like urea, sugar etc., electro-dialysis cannot be carried out.

Two electrodes are set around the parchment paper inside the water in the outer vessel and potential difference is applied through the two electrodes. The ions of the dissolved crystalloid inside the bell jar, are attracted towards the oppositely charged electrodes and thus the rate of dialysis is increased considerably.

An artificial kidney or *Haemodialyser* works according to the principle of dialysis. In a Haemodialyser there are two concentric cellophanetubes(acting as membrane). Blood flows through the inner tube while water flows through the annular space. As a result non colloidal impurities of blood are removed by diffusion. The crystalloid impurities in blood are dialysed out.

(iii) **Ultra filtration :** Since the size of the colloid particle is much smaller than the pores of an ordinary filter paper, the colloid particles easily pass through the ordinary filter paper. The pores of special membrane such as cellophane membrane are too small for the colloid particles to pass out. Consequently such filter papers are used to filter colloids. Such filter papers are called ultra filter. The rate of filtration is very slow which can be speed up by applying pressure.

• Properties of colloids :

(1) **Heterogenety :** Colloids are heterogeneous and remain suspended in the dispersion medium. Colloid particles do no settle on standing by the action of gravity though the diameter of the colloid particles is much larger than that of the particles of a true solution. This is due to (i) the Brownian movement which keeps the particles in random continuous motion, (ii) colloid particles as a whole are either positively or negatively charged. As a result the particles are repelled and are not coalesced to have diameter around 10^{-4} cm (suspension), (iii) The hydration layer prevents the colloids to come in close contact with each other. *This explains why colloid particles do not settle down on standing.*

(2) **Brownian movement :**

Colloidal particles when examined under powerful ultramicroscope, appear to be *in a state of constant rapid zig zag motion in all directions.* This was first observed by *Robert Brown* and this motion is known as Brownian movement. This is due to the bombardment of the particles of despersion medium on the colloid particles. As a result, at equilibrium the colloid particles acquire a kinetic energy which is equal to that of the kinetic energy of the particles of dispersing medium. This aquired kinetic energy of the colloid particles is exhibited in their brownian movements. The colloid particles move with a speed slower than the particles of the dispersing medium due to their heavier mass.

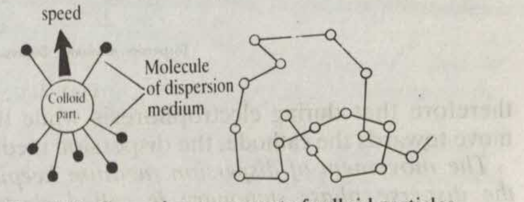


Fig. 8.19 : Brownian movement of colloid particles

Brownian movement depends on the viscosity. Increasing viscosity of the medium results in a slowing down of the Brownian movement. Again, smaller the size of the colloid particles, rapid is the movement.

(3) **Electrical properties :**

Beside Brownian movement the stability of colloid particle is attributed to the electrical charge contained in them. Unlike electrolyte, colloids are either fully positively charged or negatively charged. The like charged particles repel each other and do not coagulate to larger particles. The evidence of the presence of charge in colloids can be demonstrated by *electrophoresis* and *electro-osmosis*.

(a) **Electrophoresis or Cataphoresis :**

The platinum electrodes are dipped in a hydrophobic sol taken in a U-tube. A small amount of water sufficient to cover the platinum foil is taken. A large potential difference is then applied between the electrodes. It is observed that the colloidal particles move either towards the cathode or towards the anode, depending upon the charge they bear. The movement of the particles under the influence of electric field is usually observed by the ultra microscope. In the figure we see as the potential difference is applied between the electrodes, the negatively charged colloid particles move towards the anode. In practice it is observed that the boundary line between the colloid and the water begins to move. This movement of the boundary line gives an idea of the nature of the charge on the colloid particle.

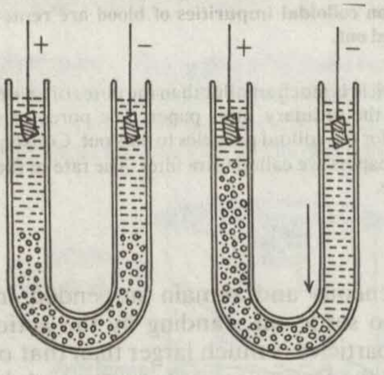


Fig. 8.20 : Electro phoresis

This movement of the colloid particles under the influence of electric field is called electrophoresis. Positively charged colloid particles move towards the cathode (cataphoresis) and the negatively charged particles move towards anode (anaphoresis).

(b) **Electro-osmosis :** We know that a colloidal solution is electrically neutral. Consequently it is logical to conclude that the charge on the disperse phase must be balanced by an equal and opposite charge on the dispersion medium. It follows therefore that during electrophoresis while the particles of the dispersed phase move towards the cathode, the dispersion medium must move towards the anode.

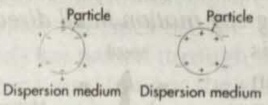


Fig 8·21 :

The movement of dispersion medium keeping the disperse phase stationary is called electro-osmosis. The following arrangement exibits electro-osmosis in a simple way. Clay is negatively charged colloid. Porous diaphragm made of clay is fixed in a U-tube and kept in it as shown in the figure. Water in contact with it must be positively charged. When electric current is passed through it, the water will be found to move away from the anode and will move towards the cathode.

(c) **Streaming and sedimentation potential :** Both in electrophoresis and in electro-osmosis, potential difference of electricity is responsible for the development of motion. In the reverse effects, motion can develop a potential difference.

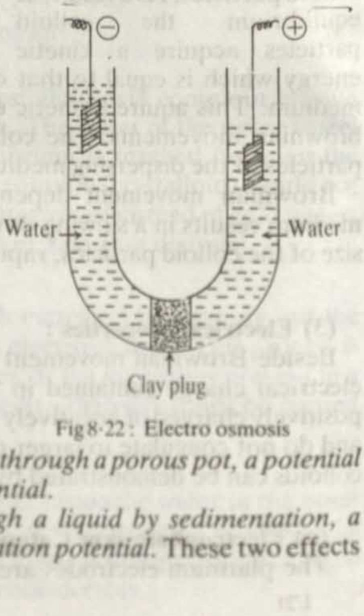


Fig 8·22 : Electro osmosis

When a liquid is forced through a capillary tube or through a porous pot, a potential difference is set up. This is known as streaming potential.

Again if solid particles are made to pass through a liquid by sedimentation, a potential difference is set up which is called sedimentation potential. These two effects are collectively called *electro kinetic phenomenon*.

(4) **Optical properties :** Colloid particles are so small that they are not visible under ordinary microscope, but their presence can be visualised by optical means. If a strong beam of light is passed through a medium containing particles of large size (10 Å—1000 Å), the medium becomes at once filled with coloured specks of light due to the scattered light from colloid particles. This phenomenon of scattering of light by particles was studied by *J. Tyndal* (1869) and is called *tyndal effect*. True solutions, do not exhibit this effect—they are optically clear. Colloid particles, on the other hand scatter the light which confirms their presence. It is observed that the intensity of the scattered light depends upon the difference of the refractive indices of the medium and the suspended particles. Larger is the difference, the greater is the tyndal effect. *This explains why the lyophobic sols give more pronounced tyndal effect than the lyophilic colloids.*

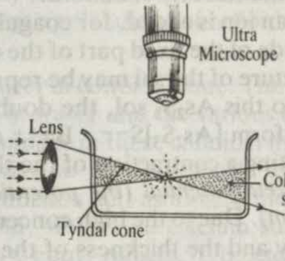


Fig 8·23 : Tyndal effect

By Tyndal effect it is possible to distinguish between colloidal state, and a true solution. It is extensively used to test the purity of the gas mixture of SO_2 and air before it is passed into the catalyst chamber, in the manufacture of H_2SO_4 by contact process.

(5) **Coagulation or flocculation :** In aqueous medium traces of electrolytes are essential for the stability of colloid but if excess of electrolyte is added, the colloid particles form aggregate and are precipitated. Thus,

Coagulation is a phenomenon of precipitation of colloid particles due to aggregation by the addition of an electrolyte. If the precipitated colloids float on the medium instead of settling down, it is called flocculation.

Coagulation means death of a colloid. Thus when a few drops of acid is added to milk it becomes caesin. In this case the colloidal milk is being coagulated by the acid to form caesin.

Schulze-Hurdy valency rule :

The influence of the charge and the valency of the added ion on the coagulation of colloid was studied by Schulze and Hardy. According to them,—

(i) In the coagulation of colloids, the ions carrying opposite charges to that of the colloid particles are most effective.

(ii) The higher the valency of the added ion, the greater is the effective power of the coagulation of the electrolyte and smaller is the amount of electrolyte required to coagulate a given amount of colloid in a given time e.g., the coagulation power of

$$Al^{3+} > Mg^{2+} > Na^{+} \text{ and } PO^{3-} > SO_4^{2-} > Cl^{-}.$$

(iii) The influence of the valency of the added ion is like geometrical proportion $1 : m : m^2$ for mono, di, and trivalent ions, where m has a value of 16 to 32. Thus if the coagulating power of $Na^{+} = 1$ then for $Mg^{++} = 32$ and for $Al^{+++} = (32)^2 = 1024$. This rule can clearly *explain why Alum is used but not common salt in the coagulation of colloidal impurities in the purification of drinking water.*

Mechanism of coagulation : *Von Helmholtz* proposed that there is an electrical double layer between the solid colloidal particle and the surrounding dispersion medium. According to *Stern* the double layer is in 2 parts—the first one, a single ion thickness which is fixed to the solid surface. The second part bearing opposite charge is diffused and extends some distance in the liquid phase. Thus a colloid with its accompanying diffused layer when approaches the other, there is a considerable repulsion among similar charges and the particles are prevented from coalescing. This explains the stability of colloid.

Now when an ion is added, for coagulation of the above colloid, it is absorbed on the solution side of the fixed part of the double layer. When As_2S_3 sol is peptised by H_2S, the structure of the sol may be represented as $[As_2S_3]S^{--} \vdots 2H^+$. When $BaCl_2$ sol is added to this As_2S_3 sol, the double layer containing H^+ ions is replaced by Ba^{++} ions to form $[As_2S_3]S^{--} \vdots Ba^{++}$ and H^+ ions then pass into the bulk of the solution effecting a contraction of the thickness of the diffused layer thus lowering the value of *zeta potential (the potential between the fixed portion and the freely moving portion)*. Due to the high concentration of the Ba^{++} ions in the solution, the charge density and the thickness of the double layer is decreased. Two As_2S_3 sols can now approach quite close and the size becomes bigger and thus As_2S_3 sol is coagulated.

(6) **Adsorption :** Colloid particles possess high power of adsorption because of their larger surface area for a given mass of substance. As their large surface area is exposed to the surrounding medium, colloidal particles are strong adsorbers. One volume of finely divided palladium adsorbs nearly 1000 volumes of H_2.

(7) **Protection :** The stability of hydrophobic sols are increased in presence of a small amount of hydrophilic sol. At this condition the hydrophobic sols are not coagulated readily by the addition of an electrolyte. As for example, if a little gelatine is added to gold sol, it is no longer coagulated by NaCl. This effect of a hydrophilic sol of preventing a hydrophobic sol from coagulation on addition of an electrolyte is called *protection* and the hydrophilic sol which is added to prevent the coagulation of a hydrophobic sol is known as *protective colloid*..

Thus gum arabic is used to prevent the coagulation of inks.

The lyophobic colloids adsorbs the lyophilic colloid particles and as a result the lyophilic colloid particles form a thin film surrounding each lyophobic colloid particle. This film prevents the lyophobic particles to react with any ions of the electrolyte added and as a result prevents the coagulation.

The protective action of lyophilic sols is compared in terms of ***gold number.***

Gold number *is defined as the weight in milligrams of dry material from which lyophilic sol is prepared, which when added to 10 ml of a standard gold sol (0·0053 to 0·0058 percent) is just sufficient to prevent the colour change from red to blue on the addition of one ml of 10% solution of NaCl.* The change of colour is due to coagulation of colloid particles. Hence smaller the numerical value of gold number, the higher is the protective action. Gelatine has small gold number and is better protective agent than Haemoglobin.

Sol	Gold No
(i) Gelatine	0·005—0.01
(ii) Haemoglobin	0·030—0.07
(iii) Gum arabic	0·150—0.25
(iv) Dextrine	0·600—12

(8) **Iso-electric point :** An ampholyte is at its Iso-electric point when the concentrations of the positive and negative ions are the same.

A colloid is at its isoelectric point when it has little or no tendency to migrate in an electric field. At this point, the viscosity, solubility and some other properties of colloids markedly change. For a lyophilic sol there is a p^H when it moves to neither of the electrodes on applying electric fields. This p^H is called the iso-electric point of that colloid. At iso-electric point the sol behaves as an electrically neutral species.

- **Practical applications of colloids :**

Colloids play a significant role in our daily life as well as in industry, agriculture, medicine and biology. Some of the important applications of colloids are discussed below :—

(1) All living particles are based upon matter in colloidal state. The cells are made up mainly of colloidal particles suspended in water and the various changes which we observe in the living world are due to changes in these colloidal matters.

(2) Colloidal medicines are more effective as they are easily assimilated and absorbed by the body. Thus cod liver oil emulsion acts as tonic, colloidal antimony is used in treatment of 'Kalazar'. The gold, silver and calcium sols are used as intermuscular injections in the treatment of gout, rickets, T.B. etc. Argerol and protargol are protective silver sols. They are used in the diseases of eye. Colloidal sulphur acts as a germicide for plants.

(3) A number of foods we consume are colloids. Milk is an emulsion of fat dispersed in water. Eggs, fruit jellies, ice cream, tea in water etc., are of colloidal origin.

(4) Formation of delta at the confluence of sea and river is a direct application of colloid. The river water carries clay particles which are negatively charged colloids. As the river water meets the sea water containing electrolytes like NaCl, $MgCl_2$ etc. the fine suspensions of clay are coagulated which gradually accumulate on the river bed to form delta.

(5) A lot of industrial goods are colloidal preparations e.g., ink, paints, vernishes, plastic, glue, graphite lubricant, resins, etc.

(6) In the purification of drinking water colloidal impurities are removed by coagulating with alum. The colloidal impurities settle down and pure clean water is decanted off.

(7) Soap and detergent provides an excellent example of colloidal particles at work. Photographic industry utilises gelatine and colloidal silver.

(8) Sewage water contains colloidal impurities, which after separation by cataphoresis, forms precipitate used as manures, water being cleaned at the same time.

(9) Smoke is a negatively charged finely divided carbon in air. If this charge is removed, the carbon particles will be aggregated and settle down. This is done in *cottrell precipitator* by passing smoke through high potential difference. Carbon particles settle down at the bottom while clean gases escape through the chimney. Pollution of air by smoke can be prevented in this way. *This explains why industrial chimneys emitting smokes have charged plates.*

(10) In minor cut during shaving we use common alum to stop bleeding. This is because of the fact that alum furnishing Al^{+++} ions coagulate the blood which is a colloid and stop further flow or blood from the cut. This explains why after shaving we rub our face with alum.

8·17. Problems on solubility of matter.

1. *When 100 g of a saturated solution is evaporated at 50°C, 50 g of solid is left behind. What is the solubility of the substance at 50°C ?*

Ans : Solution = Solute + Solvent

Here 100 g = 50 g + Solvent

∴ Solvent = 100 − 50 = 50 g

∴ At 50°C, 50 g of a solute is present in 50 g of water to form a saturated solution.

∴ " 100 g of water contain $\frac{50 \times 100}{50}$ = 100 g of solute

∴ Solubility at 50°C = 100

2. *50 g of lead nirate is dissolved in 75 ml of boiled water. How much salt will be crystallised out when the temperature of the solution is brought to 20°C ? Given the solubility of $Pb(NO_3)_2$ at 20°C = 54·4.*

Ans : Solubility of $Pb(NO_3)_2$ at 20°C = 54·4 wt. of 75 ml of water = 75 g

∴ 75 g of water will dissolve $\frac{54 \cdot 4 \times 75}{100}$ = 40·8 g of lead nitrate at 20°C

∴ At 20°C, (50 − 40·8) = 9·2 g of the salt will be crystallised out.

3. *Solubility of a salt at 30°C = 40. Calculate the weight of water required to prepare a saturated solution containing 30 g of the salt at that temperature.*

Ans : Solubility of the salt at 30°C = 40

or, 40 g of the salt in 100 g water form a saturated solution

∴ 30 " " $\frac{100 \times 30}{40}$ = 75 g of water will form a saturated solution

∴ Weight of water required = 75 g.

4. *6·0 g of a salt dissolve in 30 g of water to form a saturated solution at 60°C. What is the solubility of the salt at this temperature ?*

Ans : 30 g of water contains 6·0 g of the salt

100 " " " $\frac{6 \times 100}{30}$ = 20 g of the salt

Hence solubility of the salt at 60°C = 20.

5. *Calculate the solubility of KNO_3 at 60°C from the following data :—*

(a) Weight of dry porcelain basin = 30·75 g

(b) Weight of basin + saturated solution of KNO_3 = 146·75 g

(c) Weight of basin + dry KNO_3 = 66·75 g.

Ans : Weight of dry KNO_3 crystal = 66·75 − 30·75 = 36·0 g.

Weight of the solution = 146·75 − 30·75 = 116·0 g

Weight of water = 116·0 − 36 = 80 g

Solubility of KNO_3 at 60°C = $\frac{36 \times 100}{80}$ = 45.

6. *4 g of salt is left as residue when 20 g of an unsaturated solution is evaporated at 40°C. How much salt is to be dissolved in 100 g of the same unsaturated solution to form a saturated solution, temperature remains constant. The solubility of the salt at 40°C = 40.*

Ans : 20 g solution contain 4 g salt

100 " " " $\frac{4 \times 100}{20}$ = 20 g salt

∴ Weight of water in 100 g of unsaturated solution = 100 − 20 = 80 g.

Solubility of the salt = 40

∴ 100 g of water dissolve 40 g of the salt

80 " " " $\frac{40 \times 80}{100}$ = 32 g.

80 g water contain 20 g salt.

∴ 32−20 = 12 g salt will be required to make the solution saturated.

7. *How much salt will be crystallised out when a saturated solution of 300 g of KNO_3 at 100°C is cooled to 10°C ? The solubilities of KNO_3 at 10°C and 100°C are 20 and 250 respectively.* *[W.B.H.S. 1982]*

Ans : Solubility of KNO_3 at 100°C = 250

$\therefore$ At 100°C, 100 g of water contain 250 g of KNO_3 to form a saturated solution.

$\therefore$ Weight of solution = 250 + 100 = 350 g

$\therefore$ 350 g of a saturated solution contains 100 g of water

300 " " " " $\dfrac{100 \times 300}{350} = 85{\cdot}71$ of water

$\therefore$ Weight of KNO_3 in 300 g of saturated solution = (300 − 85·71) = 214·29 g

Again at 10°C 100 g of water contain 20 g of KNO_3

" " 85·71 " " " $\dfrac{20 \times 85{\cdot}71}{100} = 17{\cdot}14$ g

$\therefore$ Weight of crystallised KNO_3 at 10°C = (214·29 − 17·14) = 197·15 g.

8. *50 g of a saturated solution of KNO_3 at 25°C contain 21 g the salt, calculate the solubility of KNO_3 at this temperature.* *[W.B.H.S. 1984]*

Ans : Weight of the saturated solution of KNO_3 = 50 g

Weight of solid KNO_3 = 21 g

$\therefore$ Weight of water = 50 − 21 = 29 g.

$\therefore$ 29 g of water contain 21 g of solid at 25°C to form a saturated solution.

$\therefore$ Solubility of KNO_3 at 25°C = $\dfrac{21 \times 100}{29} = 72{\cdot}4$

9. *The solubility of a salt at 30°C = 45. Calculate the weight of water required to prepare 90 g of a saturated solution of the salt.*

Ans : 100 g of water is required to prepare a saturated solution of 45 g of salt.

$\therefore$ Weight of water required to prepare a saturate solution of 90 g salt = $\dfrac{100 \times 90}{45} = 200$ g

Hence 200 g of water will be required to prepare a saturated solution of 90 g of the salt at 30°C.

• Problems on water of crystallisation.

10. *On heating 0·1 g of a hydrated crystal 0·0512 g of water escape and the solid becomes anhydrous. The molecular weight of the crystal is 246. Find the number of water of crystallisation in the solid.*

Ans : 0·1 g crystal on heating gives 0·0512 g water

$\therefore$ 246 " " " " $\dfrac{0{\cdot}0512 \times 246}{0{\cdot}1} = 126$ g of water

Let the number of water of crystallisation be n

$nH_2O = 18n$

or, $18n = 126$

$n = 7$

Hence number of water of crystallisation = 7

11. *When 24·65 g of Epsom salt is heated, 12·612 g of water is removed. Find the molecular formula of the crystal.*

Ans : Let the molecular formulation of Epsom salt be $MgSO_4, nH_2O$

Weight of $MgSO_4$ in the salt = 24·65 − 12·612 = 12·038 g

Water of crystallisation = 12·612 g

Mol. weight of $MgSO_4$ = 24 + 32 + 64 = 120

" " " H_2O = 18

$$\frac{\text{Weight of } MgSO_4}{\text{Weight of water}} = \frac{1 \times \text{Mol. Wt of } MgSO_4}{n \times \text{Mol. wt of } H_2O}$$

or, $\frac{12\cdot038\text{ g}}{12\cdot612\text{ g}} = \frac{1 \times 120}{n \times 18}$

or, $n = \frac{120 \times 12\cdot612}{18 \times 12\cdot038} \approx 7$

∴ Mol. formula of Epsom salt = $MgSO_4, 7H_2O$

12. *0·6398 g of dry copper sulphate is obtained when 1·0 g of hydrated copper sulphate is heated. Calculate number of water of crystallisation contain in the molecule.* *[W.B.H.S. 1984]*

Ans : Weight of hydrated copper sulphate = 1·0 g
" " anhydrous " " = 0·6393
" " water (1·0 − 0·6393) = 0·3607 g

Mol. weight of anhydrous copper sulphate = 159·5

Number of moles of anhydrous $CuSO_4 = \frac{0\cdot6393}{159\cdot5} = 0\cdot0040081$

" " " water $= \frac{0\cdot3607}{18} = 0\cdot0200388$

Number of mole of anhydrous $CuSO_4$: Number of mole of water
= 0·0040081 : 0·0200388
= 1 : 4·999
= 1 : 5

or, the number of water of crystallisation = 5

13. *0·76 g of anhydrous salt is left when 1·5 g of hydrated $CaCl_2$ is strongly heated. Find the percentage of water in the crystal and the formula of the hydrated crystals.* *[W.B.H.S. 1968]*

Ans : Weight of water of crystallisation = (1·5 − 0·76) = 0·74 g

100 g of hydrated $CaCl_2$ contain $\frac{0\cdot74 \times 100}{1\cdot5} = 49\cdot33$ g of water

∴ % of water = 49·33

Mol. wt. of anhydrous $CaCl_2 = 111$

0·76 g of anhydrous $CaCl_2$ contain 0·74 g water

111 " " " " " $\frac{0\cdot74 \times 111}{0\cdot76} = 108$ g.

Number of water of crystallisation $= \frac{108}{18} = 6$

∴ Mol. formula of the hydrated crystals = $CaCl_2, 6H_2O$

14. *A hydrated bivalent metal sulphate contains 51·2% water of crystallisation. The atomic weight of the metal = 24. Calculate the number of water of crystallisation.* *[A.I.H.S. 1988]*

Ans : Let the mol. formula of the hydrated metal sulphate be MSO_4, nH_2O

Mol. wt. of the hydrated salt = $120 + 18n$

$(120 + 18n)$ g of the hydrated salt contains $18n$ g of water

100 " " " " " $\frac{18n \times 100}{120 + 18n}$ " "

By question,

$\frac{18n \times 100}{120 + 18n} = 51\cdot2$ or, $n = 7$

∴ Number of water of crystallisation = 7.

15. *Hydrated $BaCl_2$ contains 14·73% water of crystallisation. Find the decrease in weight when 25 g of hydrated $BaCl_2$ is strongly heated. Deduce the mol formula of the crystal.*

Ans : 25 g of hydrated $BaCl_2$ contains $\frac{14\cdot73 \times 25}{100} = 3\cdot6825$ g of water

This weight will be decreased. Hence the decrease in weight = $3{\cdot}6825$ g.
Mol. wt. of hydrated $BaCl_2 = 208{\cdot}4 + 18n$

100 g of the hydrated salt contain $\dfrac{18n \times 100}{208{\cdot}4 + 18n}$ g of water.

According to the given condition,

$$\frac{18n \times 100}{208{\cdot}4 + 18n} = 14{\cdot}73$$

$$or,\ n = 2$$

The mol. formula = $BaCl_2, 2H_2O$

• Problems on vapour pressure, elevation of B.P., depression of F.P. and osmotic pressure :

16. *A solution of glucose is prepared by dissolving 34 g in 500 g of water. Find the (i) vapour pressure of the solution at 290K, (ii) osmotic pressure at 290K, (iii) boiling point of the solution, (iv) freezing point of the solution. The vapour pressure of water at 290K is 0·022 atmos.* (K_b=0·52K kg mol^{-1} and K_f = 1·86K kg mol^{-1})

Ans : (i) We know $\dfrac{P^\circ_A - P_A}{P^\circ_A} = \dfrac{n}{n+N}$

Where, P_A = Vapour pressure of solution, n = Number of moles of solute.
P°_A = Vapour pressure of solvent, N = Number of moles of solvent.
No. of mole of solvent (N) = 500/18 = 27·8, No. of moles of glucose
(n) = 34/180 = 0·189, 0·022 atmos = 0·022 × 760 = 16·72 mm.

$$\text{or, } \frac{16{\cdot}72 - P_A}{16{\cdot}72} = \frac{0{\cdot}189}{0{\cdot}189 + 27{\cdot}8} = \frac{0{\cdot}189}{27{\cdot}989} = 0{\cdot}00675$$

$$\text{or, } 16{\cdot}72 - P_A = 16{\cdot}72 \times 0{\cdot}00675$$

$$\text{or, } 16{\cdot}72 - P_A = 0{\cdot}1128 \qquad \text{or, } P_A = 16{\cdot}6 \text{ mm.}$$

(ii) We know that osmotic pressure $\pi = \dfrac{nRT}{V}$ here $n = 0{\cdot}189$, $V = 500$ ml $= 0{\cdot}5$ lit.

$$\text{or, } \pi = \frac{0{\cdot}189 \times 0{\cdot}082 \times 290}{0{\cdot}5} = 8{\cdot}98 \text{ atmos}$$

(iii) m = molarity of glucose = $\dfrac{34 \times 1000}{500 \times 180} = 0{\cdot}378$

$\triangle T = K_b m$
$\triangle T = 0{\cdot}52 \times 0{\cdot}378 = 0{\cdot}196$K.
Boiling point of water = 100°C = 373K
Boiling point of solution = 373 + 0·196 = 373·196K

(iv) $\triangle T_f = K_f \cdot m.$ m = molarity of glucose = $\dfrac{34 \times 1000}{800 \times 180} = 0{\cdot}378$

$\therefore\ \triangle T_f = 1{\cdot}86 \times 0{\cdot}378 = 0{\cdot}703$K
Freezing point of water = 0°C = 273K
$\therefore$ Freezing point of soln = 273 − 0·703 = 272·29K.

17. *The vapour pressure of a 12% aqueous solution of a non volatile and non electrolyte at 100°C is 745·1 mm. Calculate the molecular weight of the solute.*

Ans : Mass of the solute = 12 g
Mass of water = 100 − 12 = 88 g.

According to Raoult's law.

$\dfrac{P^\circ_A - P_A}{P^\circ_A} = \dfrac{\text{mole of solute}}{\text{mole of solvent}}$ give here P°_A = 760 mm and P_A = 745·1 mm.

or, $\dfrac{760 - 745{\cdot}1}{760} = \dfrac{12/M}{88/18}$ M = molecular wt. of the solute

$$\text{or,}\quad \frac{14{\cdot}9}{760} = \frac{12/M}{4{\cdot}89}$$

$$\text{or,}\quad 0{\cdot}019 = \frac{12/M}{4{\cdot}89}$$

$$\text{or,}\quad M = 129{\cdot}17$$

18. *The boiling point of a solvent is 80·2°C. 0·419 g of the solute being dissolved in 75 g of the solvent the boiling point of the solution becomes 80·256°C. The molecular wt. of the solute is 252·4. Find the molal elevation constant.*

Ans : $\triangle T_b = K_b m$. Here $m = \dfrac{0{\cdot}419 \times 1000}{252{\cdot}4 \times 75} = 0{\cdot}022 \qquad T_b = 80{\cdot}256 - 80{\cdot}2 = 0{\cdot}056$

$$\therefore K_b = \frac{0{\cdot}056}{0{\cdot}022} = 2{\cdot}54$$

19. *25·6 g of sulphur is dissolved in 1000 g of napthalene. At this the depression of freeing point becomes 0·68°C The melting point of napthalene is 80·1°C.* K_f for napthalene = $6{\cdot}8\text{K kg mol}^{-1}$. Find the formula of sulphur.

Ans : $\triangle T_f = K_f.\, m$. Let the molecular wt. of sulphur = M

$\therefore$ Molarity of the soln. $m = \dfrac{25{\cdot}6}{M}$

$\triangle T_f = 0{\cdot}68. \qquad K_f = 6{\cdot}8\text{K kg mol}^{-1}$

$$\text{or, } 0{\cdot}68 = 6{\cdot}8 \times \frac{25{\cdot}6}{M}$$

$$\text{or, } M = \frac{6{\cdot}8 \times 25{\cdot}6}{0{\cdot}68} = 256. \quad \text{Atomic wt. of } S = 32$$

$$\therefore \text{Atomicity of } S = \frac{256}{32} = 8. \quad \therefore \text{The formula of sulpher} = S_8$$

20. *A solution containing 18 g of a solute per litre, gives an osmotic pressure = 2·39 atmosphere at 27°C . Find the molecular weight of the solute. (R = 0·082 litre atmos* $mol^{-1}K^{-1}$.

Ans : $\pi = \dfrac{n_B RT}{V}$ Where π osmotic pressure of solute = 2·39 atmos.

n_B = moles of solute = $\dfrac{18}{M}$ (M = molecular wt.)

R = 0·082, V = 1 litre, T = 273 + 27 = 300K

$$\therefore 2{\cdot}39 = \frac{18 \times 0{\cdot}082 \times 300}{M \times 1}$$

$$\text{or, } M = \frac{18 \times 0{\cdot}082 \times 300}{2{\cdot}39} = 185{\cdot}27$$

21. *Find the osmotic pressure of a soln containing 6·42 g of sucrose per litre at 127 °C. Molecular wt. of sucrose = 342. R = 0·082 litre atmos* $mol^{-1}K^{-1}$

Ans : $\pi = \dfrac{n_B RT}{V}$ Here π = osmotic pressure of soln.

n_B = moles of solute = $\dfrac{6{\cdot}42}{342} = 0{\cdot}019$

T = 127 + 273 = 400 K. $R = 0{\cdot}082$; $V = 1$ litre

$$\pi = \frac{0{\cdot}019 \times 0{\cdot}082 \times 400}{1}$$

$$= 0{\cdot}6232 \text{ atmos.}$$

22. *The vapour pressure of pure benzene at certain temperature is 640 mm Hg. A non-volatile solute weighing 2·175 g is added to 39·0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular wt. of the solute ?* *[I.I.T. '90]*

Ans : According to Raoult's law—

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{n}{n+N}\cdot \text{ Here } P_A^0 = 640\,\text{mm}, P_A = 600\,\text{mm}, n = 2{\cdot}175/\text{M}, N = 39/78.$$

M is molecular weight of the solute.

Substituting the value—

$$\frac{640-600}{640} = \frac{2{\cdot}175/\text{M}}{2{\cdot}175/\text{M} + 39/78}$$

$$\text{or, } \frac{1}{16} = \frac{2{\cdot}175}{2{\cdot}175 + 0{\cdot}5\,\text{M}} \quad \text{or, } \text{M} = 65{\cdot}25$$

23. *The vapour pressure of pure benzene at 25 °C is 639·7 mm of Hg and the vapour pressure of a solution of a solute in benzene at the same temperature is 631·9 mm of Hg. Calculate the molality of the solution.* *[I.I.T. '81]*

Ans ; Let the molality of the solution = m

i.e., the solution contains 'm' moles of solute in 1000 g of benzene.

Vapour pressure of benzene $P_A^0 = 639{\cdot}7$ mm

Vapour pressure of solution $P_A = 631{\cdot}9$ mm

No. of moles of benzene $= \frac{1000}{78}$ (mol. wt. of benzene = 78)

Moles of solute $n = ?$

Substituting the values in Roult's eq.

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{n}{N} \quad \text{or, } \frac{639{\cdot}7 - 631{\cdot}9}{639{\cdot}7} = \frac{n}{1000/78}$$

$$\text{or, } \frac{7{\cdot}8}{639{\cdot}7} = \frac{78n}{1000}$$

$$\text{or, } n = \frac{7{\cdot}8 \times 1000}{639{\cdot}7 \times 78} \quad \text{or, } n = 0{\cdot}156$$

Hence the molality of the soln = 0·156 mol kg^{-1}

24. *The vapour pressure of a dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mm of Hg at 373 K. Calculate the molality of the solution.* *[I.I.T. '89]*

Ans : From Raoult's law we get—

$$P_A = P_A^0 \times X_A$$

When P_A = vapour pressure of solvent in solution = 750 mm

P_A^0 = vapour pressure of pure solvent = 760 mm

X_A = mole fraction of the solvent.

$$\therefore \; X_A = \frac{P_A}{P_A^0} = \frac{750}{760} = 0{\cdot}9868$$

Let X_B = mole fraction of the solute.

$\therefore$ $X_A + X_B = 1$ or, $X_B = 1 - X_A$

or, $X_B = 1 - 0{\cdot}9868 = 0{\cdot}0132$

Hence, molality of the solution

$$\frac{\text{mole fraction of } X_B}{\text{mole fraction of } X_A} = \frac{\text{mole of solute}}{\text{mole of solvent}} = \frac{n}{N} = \frac{0{\cdot}0132}{0{\cdot}9868}$$

$\therefore$ In 0·9868 moles of water glucose present 0·0132 mole

In $\frac{1000}{18}$ mole of water glucose present $\frac{0{\cdot}0132 \times 1000}{0{\cdot}9868 \times 18} = 0{\cdot}743$ mole

$\therefore$ Molality = 0·743 mol kg^{-1}

25. *The boiling point of a solution of 0·105 g of a substance in 15·84 g of ether was found to be 0·1°C higher than that of pure ether. What is the molecular wt. of the substance ? Molal elevation constant of ether per 100 g = 21·6* *[MLNR '91]*

Ans : We know $M = \dfrac{100 \times K_b \times w}{\Delta T_b \times W}$

Here $K_b = 21{\cdot}6$, $\Delta T_b = 0{\cdot}1°C$, $w = 0{\cdot}105$ g, $W = 15{\cdot}84$ g

$$\therefore\ M = \frac{100 \times 21{\cdot}6 \times 0{\cdot}105}{0{\cdot}1 \times 15{\cdot}84} = 143{\cdot}18$$

26. *The degree of dissociation of $Ca(NO_3)_2$ in dilute aqueous solution containing 7 g of the salt in 100 g of water at 100° C is 70%. If the vapour pressure of water at 100° C is 760 mm, calculate the vapour pressure of the solution.* *[I.I.T. '91]*

Ans : Let 1 mole of $Ca(NO_3)_2$ is taken initially. Degree of dissociation of $Ca(NO_3)_2$ = 70/100=0·7. The ionisation of $Ca(NO_2)_2$ is

$$\begin{array}{llcccc} & Ca(NO_3)_2 & \rightleftharpoons & Ca^{++} & + & 2NO_3^- \\ \text{At start} & \text{1 mole} & & 0 & & 0 \\ \text{At equilibrium} & (1-0{\cdot}7)\text{ mole} & & 0{\cdot}7\text{ mole} & & 2\times0{\cdot}7\text{ mole} \end{array}$$

∴ At equilibrium the total number of moles in the solurion

$$= (1-0{\cdot}7) + 0{\cdot}7 + 2 \times 0{\cdot}7 = 2{\cdot}4 \text{ moles}$$

$$7\text{ g of }Ca(NO_3)_2 = \frac{7}{164}\text{ mole of }Ca(NO_3)_2$$

$$\therefore\ \text{The No. of moles of solute in soln. containing 7 g of salt} = \frac{2{\cdot}4\times7}{164}$$

$$= 0{\cdot}102 = n$$

$$\text{No. of moles of water} = \frac{100}{18} = 5{\cdot}55 = N$$

Applying Raoult's law,

$$\frac{P^{\circ}_A - P_A}{P^{\circ}_A} = \frac{n}{n+N}$$

$$\text{or,}\quad \frac{760 - P_A}{760} = \frac{0{\cdot}102}{0{\cdot}102 + 5{\cdot}55}$$

$$\text{or,}\quad \frac{760 - P_A}{760} = 0{\cdot}018$$

or, $P_A = 760 - 760 \times 0{\cdot}018 = 746{\cdot}3$ mm.

27. *Addition of 0·643 g of a compound to 50 ml of benzene (density 0·879 g/ml) lowers the freezing point from 5·51°C to 5·03°C. If K_f for benzene is 5·12 K. kg mole^{-1}. Calculate the molar mass of the compound.* *[I.I.T. '92]*

Ans : Weight of benzene = 0·879 × 50 = 43·95 g

Let, M be the molar mass of the compound

$\Delta T_f = 5{\cdot}51 - 5{\cdot}03 = 0{\cdot}48$

Applying the formula $\Delta T_f = \dfrac{K_f \times \text{Weight of solute} \times 1000}{\text{Weight of solvent} \times \text{mole weight of solute}}$

$$\text{or,}\quad 0{\cdot}48 = \frac{5{\cdot}12 \times 0{\cdot}643 \times 1000}{43{\cdot}95 \times M}$$

$$\text{or,}\quad M = \frac{5{\cdot}12 \times 0{\cdot}643 \times 1000}{43{\cdot}95 \times 0{\cdot}48}$$

• Exercises •

1. What is solution ? What do you understand by solute and solvent ? Express the relation between solute, solvent and solution.

2. What are the characteristics of a solution ? Mention the similarities and dissimilarities between solution and compound.

3. What do you understand by saturated and unsaturated solutions ? *[W.B.H.S. '91 (T) '81]*

4. What is supersaturated solution ? Describe how would you prepare a super saturated solution of sodium thiosulphate ? What happens when a small crystal of sodium thiosulphate is added to its supersaturated solution ? *[W.B.H.S. '83]*

5. Describe how would you prepare a saturated solutions of blue vitriol at room temperature ? What is the effect of temperature on a saturated solution ?

6. Suggest simple laboratory tests by which you could determine if a solution is unsaturated, saturated or supersaturated. Explain why your suggestions would distinguish between the different classifications. *[Jt. Ent. '93]*

7. Describe the mechanism of dissolution of
(a) polar solute in a polar solvent,
(b) polar covalent solute in polar solvent,
(c) non-polar solute in water.

8. Predict whether the following substances will form solution—(i) methane and water *[Jt. Ent. '91]*, (ii) HBr and water *[Jt. Ent. '91]*, (iii) sugar and water, (iv) NaCl and benzene.

9. What is solubility ? What is its difference from solubility product ?

10. (a) What is meant by the statement—'The solubility of KNO_3 at 40°C is 65' ? *[W.B.H.S. '92]*

(b) Describe how would you determine the solubility of blue vitriol at room temperature ? Why is it essential to mention the temperature in expressing the solubility of a substance ?

11. Describe how the solubility of a salt can be determined at (a) a temperature lower than the room temperature, (b) a temperature higher than the room temperature.

12. (a) Which of the following has least effect on the solubility of a solid in water ?
(i) Nature of solute, (ii) temperature, (iii) pressure. *[Jt. Ent. '93]*

13. What is solubility curve ? How would you use solubility curve for separation of sodium chloride and potassium chloride present in a mixture of the two ? *[Jt. Ent. '93]*

14. (a) How do the solubilities of nitre, common salt and Glauber's salt change with the rise of temperatures ?

(b) A hot mixed solution of nitre and common salt is allowed to cool. Which of the salts will first separate out from the solution ?

15. A salt dissolves in water to form a saturated solution at room temperature with the evolution of heat. State giving reasons the effect of temperature on the solubility of this salt. *[Jt. Ent. '90]*

16. Give the utility of solubility curve. What informations would you get from the solubility curve ? Explain the solubility curve of Na_2SO_4, $10H_2O$. *[H.S. '92]*

17. (i) Illustrate with examples, the relation of solubility with the temperature.

(ii) Show with diagram, the nature of the solubility curves of NaCl and Na_2SO_4, $10H_2O$. What informations would you get regarding the solubility of the two salts in water from these curves ? *[Jt. Ent. '80]*

18. Define the terms crystal and crystallisation. What is fractional crystallisation ? Describe the different processes of crystallisation.

19. What is water of crystallisation ? Does water of crystallisation play any role in determining the properties of crystals ? *[H.S. '93]*

20. How could you find the number of water of crystallisation of blue vitriol ?
Mention the practical applications of fractional crystallisation.

21. (a) What do you understand by efflorescence ? Give an example of an efflorescent substance ? *[H.S. '90]*

(b) What do you understand by deliquescense ? Give an example of an deliquescent substance ? Mention the causes of these phenomenon ?

22. Distinguish between—
(i) Saturated solution and supersaturated solution *[Jt. Ent. '93]*, (ii) Water of crystallisation and water of constitution *[Jt. Ent. '93]*, (iii) Hydrophobic and hydrophilic *[Jt. Ent. '93]*, (iv) Deliquescent and hygroscopic substance *[Jt. Ent. '94]*.

23. Define Colloidal solution ? What do you mean by dispersed phase, dispersion medium and colloidal state.

24. Describe with examples the general methods of preparation of Colloids. State the important properties of Colloids. What is an aerosol ? Give two examples. *[Jt. Ent. '92]*

25. What do you understand by efflorescence and deliquescence ? Give examples of each. Explain why some crystals behave like this. *[H.S. '87]*

26. What is meant by—

(i) Peptization, (ii) Tyndal effect, (iii) Brownian movement, (iv) Coagulation, (v) Gold number.

27. The solubility of ammonia in water at constant temperature and pressure is decreased in presence of caustic soda in solution. How can you explain this phenomenon in the light of chemical equilibrium concept ? *[H.S. '94]*

28. Explain why—

(i) Polar substance generally dissolves is polar solvent but not in non polar solvent.

(ii) The solubility of Glauber's salt at first rises up to 32·38°C but after that decreases.

(iii) A solution exhibits many properties of a compound, but inspite of that it is a mixture.

(iv) The Colloid particles move towards the electrode when it is brought into an electric field.

(v) When kept exposed to air, Na_2CO_3, $10H_2O$ acts as an efflorescent but $MgCl_2$, $6H_2O$ acts as a deliquescent. *[Jt. Ent. '88]*

(vi) The solubility of Glauber's salt is maximum at 32. 38°C.

(vii) An unsaturated or a super saturated solution of a solid, can not remain in contact with the solid solute.

(viii) Sodium chloride dissolves in water but not in benzene.

(ix) Water is a versatile solvent.

(x) In minor cuts during shaving we use common alum to stop bleeding.

(xi) The industrial chimneys emitting smoke have charged plates.

(xii) The solubility of sugar in a cup of water will not be same at Darjeeling and Calcutta.

(xiii) Colloid particles do not settle down on standing.

(xiv) Lyophobic sol give more pronounced tyndal effect than the lyophilic sols

(xv) Alums, but not common salt is used for the coagulation of colloidal inpurities of drinking water.

29. Explain how would you use solubility curve in the separation of KCl and $KClO_3$ from a mixture of the two.

30. State Raoult's law and explain how molecular weight of a dissolved solute can be found out by applying this law.

31. Distinguish between (a) true solution and colloidal solution. *[H.S. '90]*. Mention the differences between lyophobic and lyophilic sols.

32. Write short notes on (a) Dialysis, (b) Electrophoresis, (c) Coagalution and its mechanism.

Numerical problems :

1. The solubilities of KNO_3 at 20°C and 70°C are 30 and 140 respectively. At 70°C, 75 g of water is made saturated with nitre. If the temperature of this saturated solution is brought down to 20°C, how much nitre will crystallise out from the solution ? [**Ans.** 82·5 g] *[W.B.H.S. '89]*

2. 1·0 g of a metal (at wt 56) produces 4·9642 g of hydrated sulphate. 1·0 g of this hydrated sulphate on heating liberates 0·4532 g of water. What is the simplest formula of the hydrated sulphate ?

[**Ans.** $MnSO_4$, $7H_2O$] *[Jt. Ent. '88, '93]*

3. 69 ml of 0·25 (N) H_2SO_4 is required to neutralise 4·125 g of a saturated solution of a metallic carbonate at 27°C. If the equivalent weight of the metallic carbonate is 53, find its solubility at 27°C.

[*Hint* : 69 ml of 0·25 (N) $H_2SO_4 \equiv \frac{69 \times 0{\cdot}25}{1000} = 0{\cdot}01725$ gram eq. of H_2SO_4

$\equiv 0{\cdot}01725$ gram eq. of Na_2CO_3

$\equiv 0{\cdot}01725 \times 53 = 0{\cdot}914$ g of Na_2CO_3

Amount of water $= 4{\cdot}125 - 0{\cdot}914 = 3{\cdot}211$ g Solubility at 27°C $= \frac{0{\cdot}914 \times 100}{3{\cdot}211} = 28{\cdot}46$]

4. 0·5 g of a crystalline salt gives out 0·256 g of water of crystallisation on heating and becomes anhydrous. Molecular weight of crystalline salt is 246. Find the number of molecules of water in 1 molecule of the hydrated salt. [**Ans.** 7]

5. At 20°C, 7·6 g of a saturated solution of sugar contain 5·1 g of sugar. Find out the solubility of sugar at 20°C. [**Ans.** 204] *[W.B.H.S. '93]*

6. The solubility of a salt at 30°C is 25. How much salt will be required to prepare its saturated solution of 400 g. [**Ans.** 80 g]

7. Some amount of salt is dissolved in water and a saturated solution of 75 g is obtained at 80°C. If the temperature of this solution is brought down to 30°C, how much salt will crystallise out ? Solubilities of the salt at 30°C and 80°C are 45 and 100 respectively. [**Ans.** 41·25 g]

8. At 40°C, 45 g of a solution contain 10 g of a salt. How much more of the salt is to be added to the solution at 40°C to make it saturated ? Solubility of the salt at 40°C is 55. [**Ans.** 9·25 g]

9. 0·249 g of a hydrated crystal on being heated gives 0·09 g of water and the salt becomes anhydrous. The molecular weight of the hydrated crystal is 249·5. Find the number of water of crystallisation in one molecule of the hydrated salt. [***Ans.*** 5]

10. Blue vitriol contains 36·027% of water of crystallisation

(a) How much water will be lost when 5 g of blue vitriol is heated ?

(b) The formula of blue vitriol is $CuSO_4, nH_2O$. One gram of the crystal when heated leaves a residue of 0·64 g. Find the number of water of crystallisation in blue vitriol. [***Ans.*** 1·8013 g, 5]

11. 1·582 g of anhdrous zinc sulphate is kept in moist air at 25°C. After a few days its weight is increased to 2·824 g and no further increase in weight is observed. What is the formula of the hydrated salt which is stable at 25°C. (Zn = 63·4) [***Ans.*** $ZnSO_4, 7H_2O$]

12. At 25°C, 1000 ml of a saturated solution of KNO_3 (Sp. gr = 1·332) was completely evaporated and dried, when 333 g of the anhydrous salt was obtained. Find the solubility of KNO_3 at 25°C. [***Ans.*** 33·33] *[W.B.H.S. '86]*

13. The formula of green vitriol is $FeSO_4, 7H_2O$. How much water is present in 40 g of the hydrated salt ? [Fe = 56] [***Ans.*** 18·13 g]

14. 69 ml of 1 (N) HCl is required to neutralise 16·5 g of a saturated solution of Na_2CO_3 at 25°C. Find the solubility of Na_2CO_3 at 25°C. [***Ans.*** 28·48]

15. A sugar syrup of 214·2 g contains 34·2 g of sugar ($C_{12}H_{22}O_{11}$) calculate (i) molal concentration, (ii) mole fraction of sugar in the syrup. [***Ans.*** 0·56 ; $9{\cdot}9\times10^{-3}$]

16. Calculate the osmotic pressure of 0·5% soln. of glucose at 18°C, the value of the solution constant is 0·082 1 lit atm deg^{-1} $mole^{-1}$. [***Ans.*** 0·6628 atm] [*Roorkee Eng '81*]

17. Calculate the osmotic pressure of glucose soln. containing 1·75 g in 150 ml of soln. at 17°C. [***Ans.*** 0·81 atm] [*Roorkee Eng '85*]

18. A soln. mole by dissolving 0·32 g of a new compound in 25 g of water has a freezing point of −0·021°C. Calculate the molecular wt. of the new compound (K_f = 1·86°C.) [***Ans.*** 0·201] [*MLNR '85*]

19. An aqueous soln. of glucose ($M = 180$) containing 12 g of glucose dissolved in 100 g of water was found to boil at 100·34°C while the boiling point of pure water was 100°C. Calculate the molal elevation constant for water. [***Ans.*** 0·51] [*Roorkee Eng '86*]

20. 0·48 g of an organic compound dissolved in 10·6 g of benzene lowered its freezing point by 1·8°C. Find out the molecular wt. of the compound (K_f for benzene = 5·0°K.) [***Ans.*** 125·78] [*Roorkee Eng '82*]

Objective questions :

Select the correct answer—

(i) In which mode of expression, the concentration of soln. remains independent of temperature ?
(a) Molarity, (b) Normality, (c) Formality, (d) Molality. [***Ans.*** (d)] [*I.I.T. '89*]

(ii) Sum of mole fractions of two components of a solution is always (a) more than 1, (b) less than 1, (c) Exactly 1, (d) Not fixed. [***Ans.*** (c)] [*MLWR '86*]

(iii) Colligative properties of the solution depend on (a) Nature of solute, (b) Nature of solvent (c) Number of particles present in the soln (d) Number of moles of the solvent only. [***Ans.*** (a)] [*C P M T '84*]

(iv) Which of the following 0·1 M aqueous soln. will have the lowest freezing point ? (a) K_2SO_4, (b) NaCl, (c) Urea, (d) Glucose. [***Ans.*** (a)] [*I.I.T. '89*]

(v) When glycerine is added to 1 litre of water, which of the following is observed ? (a) Water evaporates more easily, (b) the temperature of water increases, (c) The freezing point of water is lowered, (d) the viscosity of water is lowered. [***Ans.*** (c)]

(vi) The molal elevation constant is the ratio of the elevation of BP to (a) Molality, (b) Molarity, (c) Mole fraction of the solute, (d) Mole fraction of the solvent. [***Ans.*** (a)] [*C P M T '82*]

ELECTROLYSIS

9

9.1. Electrolytes.

Substances that conduct electricity with simultaneous chemical changes, either in the molten state or in aqueous solution as a result of the presence of ions are called ***Electrolytes.*** They are molten ionic compounds or solutions containing ions i.e., solutions of ionic compounds or compounds which ionise in solution. Liquid metals, however, are not regarded as electrolytes since conduction here takes place due to free electrons without any chemical change of the metal.

Examples : Acids (H_2SO_4, HCl, HNO_3 etc.), alkalies (KOH, NaOH etc.), salts ($CuSO_4$, $ZnSO_4$, $MgCl_2$ etc.)—these compounds conduct electricity either in the molten state or in aqueous solution and suffer electrolytic decomposition and new substances are formed at the electrodes.

In order to convey electric current through an electrolyte say an aqueous solution of HCl the latter is taken in a vessel called *voltameter* (Fig 9.1). Two electrodes are dipped in the solution. *Anode* is the metal rod which is connected to the positive terminal (pole) of the battery. Current, in fact, enter into the electrolyte through this electrode. It is positive electrode. *Cathode* or negative electrode is the metal rod which is joined to the negative terminal (pole) of the battery and through this current leaves the electrolyte. Substances like *Pt, Ni, Cu, Fe, Graphite, Gas carbon* etc., are used as electrodes. As soon as current enters the electrolyte, the electrolyte suffers decomposition. Thus conc. HCl forms hydrogen at the cathode and chlorine at the anode.

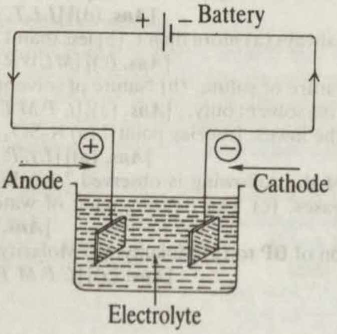


Fig 9.1 : Voltameter

$$HCl \rightleftharpoons H^+ + Cl^-$$

At Cathode :—

$H^+ + e \rightarrow H$

$H + H \rightarrow H_2 \uparrow$

At anode :—

$Cl^- - e \rightarrow Cl$

$Cl + Cl \rightarrow Cl_2 \uparrow$

- **Non-electrolytes :** *The substances which do not ionise and do not conduct current even in the molten state or in aqueous solution are called non-electrolytes.*

Most of the organic compounds belong to this category. Thus sugar, starch, urea, glycerine, petrol, kerosene etc., do not conduct current either in liquid state, molten state or in aqueous medium. These are all covalent compounds. But pure HCl although non-conductor in the liquid state, conducts current in aqueous medium. CH_3COOH behaves similarly.

- **Testing of electrical conductivity**

The following simple experiment will demonstrate whether a substance is electrolyte or non electrolyte.

Experiment : An aqueous solution of an electrolyte say sodium chloride is taken is a vessel. Two platinum electrodes are immersed in the solution. An electric bulb and a battery are connected to the electrodes in series. The bulb will glow as soon as current is passed through the circuit. This proves that an aqueous solution of sodium chloride conducts electric current. If now sodium chloride solution is replaced by a non-electrolyte say alcohol in the vessel the bulb will not glow even if current is passed by tapping the key. This proves that a non-electrolyte cannot convey current through it.

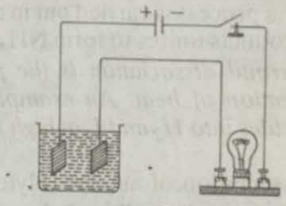


Fig. 9.2 :

- **An aqueous solution of NaCl conducts current but a solution of sugar does not.**

Sodium chloride is an ionic compound and so it is an electrolyte. The molecules of NaCl dissociate into Na^+ and Cl^- ions in the molten state or in aqueous medium. Since the ions conduct electricity, an aqueous solution of NaCl (or in molten state) is a good conductor of electricity. Sucrose or common sugar $C_{12}H_{22}O_{11}$ is a covalent compound, its molecules neither exist as ions nor dissociate into ions in aqueous medium or molten state. They exist as molecule. Hence sugar is not conductor is electricity.

9.2. Electrolysis.

Electrolysis is the process of chemical decomposition of an electrolyte either in the fused state or in an aqueous solution by the passage of electric current through it. It may also be defined as a process where electrical energy is transformed into chemical energy.

The molecules of an electrolyte in the molten state or in aqueous solution, dissociates into positively and negatively charged particles called **ions.** The process of splitting up the molecules into ions is called **ionisation.**

Ions : *Atoms or a group of atoms become charged either by accepting or losing electrons. These species carrying positive or negative charge are called ions which have no free existence, occur only in polar solvent (water). The positively charged species are called* **cations** *and the negatively charged ones are* **anions.**

When expressed in grams, the weight of ion is called **gram-ion.**

During electolysis positive ions (cations) migrate to the cathode and the negative ions (anions) to the anode. They are liberated at the respective electrode either by accepting or losing electrons. Hence electrolysis is an example of Redox reaction. *At the anode, the anions lose electrons and are discharged. Hence the process is oxidation. At the cathode, the cations in solution gain electrons to form neutral species. Thus cathode reactions are reductions.*

Example : In the fused state sodium chloride dissociates into Na^+ and Cl^- ions. On passing electric current through Pt electrode into molten sodium chloride, Na^+ ions migrate towards the cathode, and each Na^+ ion accepts an electron and gets discharged. On the other hand, the anion Cl^- ion migrates to the anode, loses electron and is liberated as chlorine gas.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At cathode :—

$$Na^+ + e \rightarrow Na \downarrow \text{ (Reduction)}$$

At anode :— $2Cl^- - 2e \rightarrow Cl_2 \uparrow$ (Oxidation)

[Loss of electron is called oxidation while gain of electron is reduction.]

9.3. Thermal dissociation and Electrolytic dissociation.

Dissociation is the process of decomposition of a molecule of an element or a compound into its constituent particles. It is a reversible process.

Thus NH_4Cl is dissociated into NH_3 and HCl on the application of heat.

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

If the process is carried out in a closed vessel and then the temperature is decreased the products unites to form NH_4Cl. This is an example of thermal dissociation.

Thermal dissociation is the process of decomposition of the molecule by the application of heat. An example of thermal dissociation is the splitting up of HI molecules into H_2 and I_2 at high temperature.

$$2HI \rightleftharpoons H_2 + I_2$$

Dissociation of an electrolyte, both strong and weak into cations and anions is called electrolytic dissociation, e.g., KCl when dissolved in water dissociates into K^+ and Cl^- ions.

$$KCl \rightleftharpoons K^+ + Cl^-$$

Comparison between Thermal and Electrolytic dissociation

Thermal dissociation	Electrolytic dissociation
1. Thermal dissociation takes place on application of heat. It does not take place at room temperature. $NH_4Cl \rightleftharpoons NH_3 + HCl$	1. Electrolytic dissociation occurs in electrolyte either in the fused state or in aqueous solution. $NaCl \rightleftharpoons Na^+ + Cl^-$
2. No medium is necessary for thermal dissociation. The compound is simply heated.	2. The substance undergoing electrolytic dissociation must either be in molten condition or dissolved in some polar solvent.
3. The original compound can be obtained by cooling the fragments.	3. The original compound can be recovered by cooling the ions in case of fused state. Evaporation of solvents completely reverts back the original electrolyte.
4. The process is reversible. Equilibrium is maintained between the reactants and the products if the reaction is carried out in a closed vessel.	4. The process is reversible. Equilibrium is maintained between the ions and the molecules except in strong electrolytes.
5. The products are neutral molecules.	5. The products are electrically charged.
6. The fragment molecules formed during thermal dissociation can be separated by diffusion, etc.	6. The ions formed during electrolytic dissociation cannot be separated by any physical means.
7. Thermal dissociation is observed in both electrolytes and non-electrolytes.	7. Electrolytic dissociation is observed only in case of electrolytes.
8. Although the process is reversible, removal of the products makes the reaction irreversible.	8. Strong electrolytes undergo complete dissociation in aqueous medium. At infinite dilution a weak electrolyte dissociates completely.

9.4. Arrhenius theory of electrolytic dissociation

The mechanism of electrolytic dissociation in the fused state as well as in aqueous medium was first put forward by Svante Arrhenius (1887). Many modifications have been made in the original concept but the basic ideas are still accepted. The theory, in its broadest out line, deals with the formation, the number and the speed of ions in a liquid or in a solution. The fundamental postulates of Arrhenius theory are as follows :—

1. *An electrolyte (acids, bases, salts etc.) in molten state or in aqueous medium dissociate into positively and negatively charged atom or group of atoms either completely or partially. These charged atoms are called ions. Positively charged ions are called cations while negatively charged ions are known as anions.*

2. *Any electrolyte gives both positively charged and negatively charged ions. The number of cations and that of anions from an electrolyte may be the same or different but the total charge on cations is exactly balanced by that on anions. Solutions of electrolytes are, therefore, electrically neutral because of this equality of opposite charges, though they contain free positive and free negative ions.*

A molecule of NaCl on ionisation form same number of Na^+ and Cl^- ions but $CaCl_2$, on ionisation, liberates one Ca^{++} ion and two Cl^- ions.

$$CaCl_2 \rightleftharpoons Ca^{++} + 2Cl^-$$

Here 1 molecule of $CaCl_2$ form one cation and two anions and the total positive charge of a cation is same as the total negative charge of two anions.

Some examples are given below :

Electrolyte	Cation	Anion	Total positive charge	Total negative charge
KCl	K^+	Cl^-	$+1$	-1
$MgCl_2$	Mg^{++}	$2Cl^-$	$+2$	$2\times(-1)=-2$
$AlCl_3$	Al^{+++}	$3Cl^-$	$+3$	$3\times(-1)=-3$
$(NH_4)_2SO_4$	$2NH_4^+$	SO_4^{--}	$2\times(+1)=2$	$1\times(-2)=-2$

3. *The physical and chemical properties of an ion and an atom of the same element are quite different.*

The atoms or the radicals are charged into cations and anions respectively by the loss and gain of electrons.

$$M - e = M^+ \text{ (Cation)}$$
$$X + e = X^- \text{ (Anion)}$$

Ion is electrically charged but atom is electrically neutral. Ions are more stable than corresponding atoms. Thus sodium catches fire when dropped into water, vigorously reacts with it liberating H_2 and forming NaOH.

$$2Na + 2H_2O = 2NaOH + H_2$$

Na^+ ion exists in aqueous medium. It does not react with water at all.

4. *A equilibrium exists between the ions of the electrolyte formed as a result of electrolytic dissociation and its un-ionised molecules.*

It is represented by the symbol $\rightleftharpoons$. This is because all the molecules of the electrolyte do not ionise completely. Some of the cations combine with anions to reform the undissociated molecules. As soon as these molecules are formed, the others suffer dissociation. The rate of dissociation into ions and the rate of formation of molecules become same or in other words an equilibrium is maintained between the ions and the molecules in molten or aqueous solution.

$$MA \rightleftharpoons M^+ + A^-$$

Applying Law of mass action $K = \dfrac{[M^+][A^-]}{[MA]}$

5. *Depending upon the degree of dissociation, electrolytes are divided into two classes.*

(a) **Strong electrolytes :** *Such electrolytes are completely ionised in a solution. The number of ions present in a solution does not depend upon dilution but upon the concentration of the solution. They include mineral acids, alkalies and salts. They give solutions of much higher conductivity than weak electrolytes.*

(b) **Weak electrolytes :** *Such electrolytes ionise in solution incompletely. They are comparatively poor conductors in solution because only a fraction of their molecules suffer ionisation.*

Examples : *Most of organic acids and bases, NH_4OH, H_2O etc.*

6. *The degree of dissociation of a weak electrolyte increases with dilution.* At infinite dilution a weak electrolyte is completely dissociated and behaves like a strong electrolyte. As the concentration of a weak electrolyte increases, the degree of dissociation decreases. Lack of complete ionisation accounts for the low conductivity of weak electrolyte especially in higher concentration.

In fact the dissociation of an electrolyte depends upon (i) *Concentration of the solutions,* (ii) *Temperature,* (iii) *Nature of electrolytes and* (iv) *Nature of the solvents.*

7. *The free ions in the solution conduct electric current.* The conductivity of a solution of an electrolyte depends upon the number of ions furnished by the molecules and not upon the number of undissociated molecules. *The number of ions furnished by dilute H_2SO_4 is much more than that given by conc. H_2SO_4. This explains why dilute H_4SO_4 is better conductor of electricity than concentrated H_2SO_4.*

8. Electric current enters through the anode into the electrolyte, flows from anode towards cathode and then returns to battery from cathode. During electrolysis the anions migrate towards anode and cations towards cathode. The anions lose their extra electrons and are converted into neutral atoms or radicals. The cations gain electrons from cathode and consequently form neutral molecules. *Hence electrolytic products are found only at the electrodes.*

9. *The molecules of an electrolyte are formed as a result of electrostatic attraction between cations and anions.* In solution the oppositely charged ions fly apart as a result of decrease of electrostatic attraction between them. The energy responsible for this is the dielectric constant of the medium. The dielectric constant of water is 80 and that of alcohol is 25 and in vacuum it is assumed to be zero. This is the reason why electrolytes ionise more in water than in alcohol.

[The force of attraction between a cation (M^+) and an anion (A^-) of an electrolyte in water is 1/80 and in alcohol it is 1/25 of the force between the ions separated by the same distance in a vacuum].

10. *Ions furnished by the electrolytes in solution do not exist in the free state. They are generally solvated.* Thus a bare proton can not exist in aqueous medium in the free state. It exists as $(H_3O)^+$ hydroxonium ion. Thus ionisation of NaCl in aqueous medium should be strictly written as follows although we seldom do so unless the particular reaction has some specific significance.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$Na^+ + xH_2O \rightleftharpoons [Na(H_2O)_x]^+$$

$$Cl^- + yH_2O \rightleftharpoons [Cl(H_2O)_y]^-$$

Overall reaction :

$$NaCl + (x + y)\,H_2O \rightleftharpoons [Na(H_2O)_x]^+ + [Cl(H_2O)_y]^-$$

11. *The passage of electric current through a solution of electrolyte, depends both on the number of ions present in solution and on their speed.*

Since strong electrolytes ionise completely in solution, the number of ions present in the solution should be proportional to the concentration of the solution. It is however observed that the conductivity is not proportional to the concentration. It is now argued that variation of ionic speed is the main cause of the effect of dilution on the conductivity of strong electrolytes. In concentrated solution, the number of ions are much greater and hence effective ionic speed decreases. On dilution with water ionic interference becomes lesser and free movements of ions are possible. Therefore the conductivity of weak electrolytes also increases with the dilution.

This idea of ionic interference is a valuable addition to the Arrhenius classical idea of electrolytic dissociation.

- **Applications of Arrhenius ionic theory :**

Various problems related to ionisation of electrolyte can be solved on the basis of above ideas. Let us deal with some problems here.

1. *Dilute H_2SO_4 is a stronger acid and better conductor than concentrated H_2SO_4.*

Dilute H_2SO_4 is stronger acid than conc. H_2SO_4 and is also better conductor of electricity. Conc. H_2SO_4 is a weak electrolyte as it dissociates to a small extent.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

The number of ions in conc. H_2SO_4 is few. But according to Ionic theory on dilution with water degree of ionisation increases and as a result number of ions becomes much greater.

$$H_2SO_4 + 2H_2O \rightleftharpoons (H_3O)_2SO_4 \rightleftharpoons 2H_3O^+ + SO_4^{--}$$

Dil. H_2SO_4 becomes strong electrolyte, ionises completely in aqueous medium. Since number of ions furnished by dil. H_2SO_4 is more than that of conc. H_2SO_4, the former is better conductor of electricity than conc. H_2SO_4. Again Arrhenius theory of acids and bases suggests that as the number of H^+ ions, i.e., H_3O^+ ions, increases, the solution becomes more acidic. The number as well as concentration of H_3O^+ ion is more in dilute. H_2SO_4 than in conc. H_2SO_4, hence dil. H_2SO_4 is a stronger acid than conc. H_2SO_4.

2. *The conductivities of hydrochloric acid and acetic acid are different.*

As HCl is a strong electrolyte, it completely ionises in aqueous medium to form H_3O^+ and Cl^- ions. The ions in the molten state or in aqueous solution actually conduct current and as the number of ions furnished by the electrolyte in solution increases, the conductivity of solution also increases.

$$HCl + H_2O \rightleftharpoons H_3OCl \rightleftharpoons H_3O^+ + Cl^-$$

Acetic acid, on the other hand, is a weak electrolyte, dissociates incompletely in water. Consequently it furnishes less number of ions in aqueous solution. Hence, while HCl is a good conductor of electricity, CH_3COOH is a very poor conductor.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

The number of ions in solution furnished by HCl is more than that of CH_3COOH, both having the same concentration. However, a dilute solution of CH_3COOH is a good conductor of electricity.

3. *Ionic compounds conduct electric current in the molten state or in aqueous medium while covalent compounds generally do not do so.*

The ionic compounds consist of oppositely charged ions held by electrostatic force to form ion pair. The ion pairs form cluster as a result of electrostatic force among the ion pairs to form crystal lattice, having characteristic structure. On heating the crystal, its lattice structure breaks or if it is dissolved in a polar solvent of sufficiently high dielectric constant (e.g. H_2O), the crystal gives rise to constituent ions. Since ions are the carrier of charges they conduct electricity. Hence all ionic compounds are good conductor of electricity. A covalent substance does not contain any ion. The solid covalent compound consists of molecular lattice unlike ionic lattice in ionic compound. Hence covalent compounds do not furnish ions and as such can not conduct electricity in aqueous medium or in the fused state (Polar covalent molecules e.g. $CHCl_3$ are however, feeble conductor).

4. *Pure HCl is a covalent compound but an aqueous solution of HCl is a good conductor of electricity.*

Pure and dry HCl is a covalent molecule. Consequently it does not ionise at all in the pure state. Hence it can not conduct electricity. But in aqueous solution it furnishes ions and conducts electricity. A covalent bond between hydrogen and chlorine atom is formed by sharing of 1 electron each from the two atoms. ($H = 1s^1$ and $Cl = 1s^2\,2s^2\,2p^6\,3s^2\,3p_x{}^2\,3p_y{}^2\,3p_z{}^1$). Hence no ion exists in the molecule of HCl. This explains why in pure state neither gaseous nor liquid HCl conducts electric current. Since chlorine is a strong electronegative atom, it attracts the electron pair formed between the H and Cl atoms towards itself. As a result chlorine atom becomes slightly negatively charged and hydrogen atom positively charged. As a result the HCl molecule becomes polar. This polar HCl molecule when comes in contact with water, the negative end of the dipole water molecule attracts the positive end of HCl i.e., H^+ ion and the positive end of the dipole water molecule attracts the negative end of HCl i.e., Cl^-. As a result of this attraction from opposite end by the dipolar water molecule, the molecule HCl is raptured to form H^+ and Cl^- ions. H^+ ions combine with lone pair of H_2O to form stable hydroxonium ion H_3O^+ in aqueous medium. Therefore dry HCl gas in water exists as H_3O^+ and Cl^- ions. Hence an aquous solution of HCl conducts electric current (Fig 9.3).

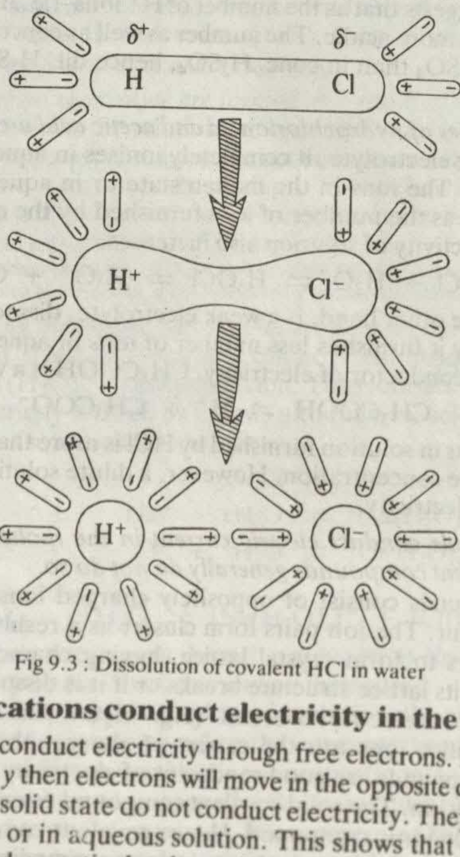


Fig 9.3 : Dissolution of covalent HCl in water

9.5. Anions and cations conduct electricity in the same direction.

Metallic conductors conduct electricity through free electrons. If current flows from the point *x* to the point *y* then electrons will move in the opposite direction from *y* to *x*. But electrolytes in the solid state do not conduct electricity. They conduct electricity only in the fused state or in aqueous solution. This shows that current is conveyed through positively and negatively charged ions in the electrolytes. The fact is demonstrated by an experiment (Fig 9.4). The electrolyte is dissolved in water and the solution is taken in a vessel called voltameter. Two platinum electrodes are immersed in the solution and connected to the two terminals of a battery. Current will flow from the positive pole to the negative pole of the battery or in other words electrons will flow from the partially immersed platinum rod acting as cathode to the anode. The cations in the solution migrate to the cathode, accept required number of electrons and are discharged at the cathode to form neutral substance. On the other side, the anions migrate to the anode, lose the extra electrons and are liberated at the anode as neutral substance. The extra electrons will come back to the positive pole of the battery through the anodic medium. It follows, therefore, that the potential difference across the two electrodes, forces the ions to move in one direction and maintains the flow of electrons from cathode to anode. As a result current flows from anode to cathode in the solution. The cations migrate to the cathode, electricity flows from anode to cathode. The anions carrying electrons migrate to the anode from the cathode. Since flow of electrons and current takes place in opposite direction, the anions carry electricity from anode to cathode.

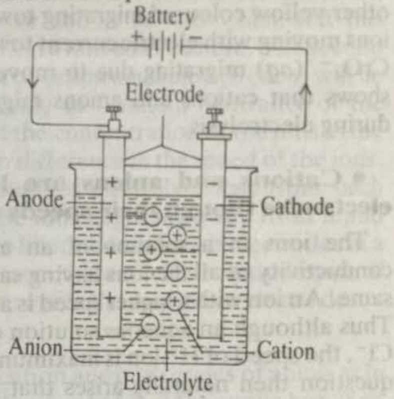


Fig. 9.4

• **Experiment :** *The cations migrate towards cathode and anions towards anode during electrolysis.*

The above statement of Arrhenius can be demonstrated by a simple experiment. A filter paper strip (8 × 3) cm is soaked with an aqueous solution of KNO_3 and is kept on a clean watch glass. The two ends of the filter paper are joined to the 15 volts battery through two clips attached to the filter paper. Copper chromate ($CuCrO_4$) is kept suspended on the KNO_3 solution at the centre of the filter paper. Electric current is now passed through the filter paper. After some time two distinct zones

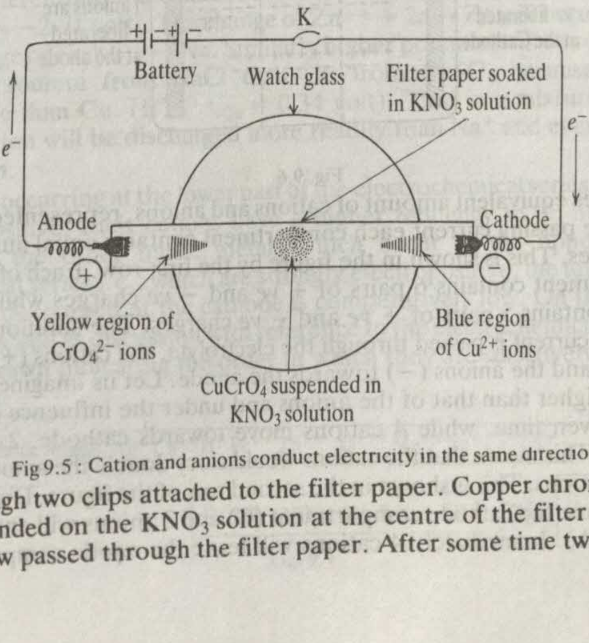

K
Battery
Watch glass
Filter paper soaked in KNO₃ solution
e⁻
e⁻
Anode
Cathode
+
−
Yellow region of CrO₄²⁻ ions
Blue region of Cu²⁺ ions
CuCrO₄ suspended in KNO₃ solution

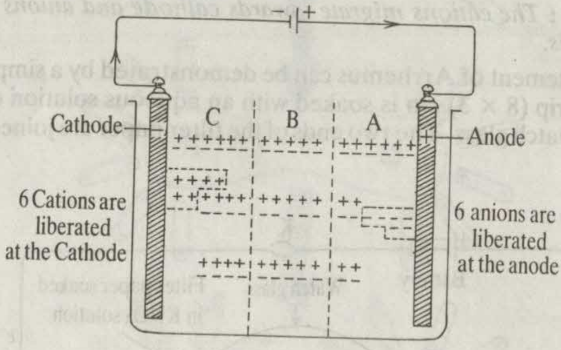
Fig 9.5 : Cation and anions conduct electricity in the same direction

will be visible on the filter paper–one blue coloured moving towards cathode and the other yellow coloured migrating towards anode. The blue zone is due to $Cu^{++}(aq)$ ions moving with electric current towards the cathode while the yellow one is due to $CrO_4^{--}(aq)$ migrating due to movement of electric current towards anode. This shows that cations and anions migrate towards cathode and anode respectively during electrolysis.

• **Cations and anions are liberated in equivalent amount at the electrodes though their speeds differ.**

The ions in a solution of an electrolyte conduct electric current. But the conductivity of all the ions having same charge and same concentration are not the same. An ion with a higher speed is a better conductor than an ion with lower speed. Thus although an aqueous solution of HCl contains three ions e.g., H^+, OH^- and Cl^-, the speed of H^+ ion is maximum and hence conducts electric current best. The question then naturally arises that if the ions having higher speed convey more current in solution, then how it is possible that equivalent quantity of cations and anions are discharged at the respective electrodes as a result of passage of current through the electrolyte. This "apparent discrepancy" can be explained with the help of Fig 9.6.

Let us consider an electrolytic cell (voltameter) imagined to be divided into three compartments—Anode compartment (A), Cathode compartment (C), and the Central compartment (B). The cell contains an uni-univalent electrolyte NaCl which discharges equivalent amount of cations and anions, represented by + and − charges. Before passing current each compartment contains equal number of + *ve* and − *ve* charges. This is shown in the figure by the first row. Each of cathode and anode compartment contains 6 pairs of + *ve* and − *ve* charges while the central compatment contains 5 pairs of + *ve* and − *ve* charges. The solution is therefore neutral. Now if current is passed through the electrolyte, the cations (+) will migrate to the cathode and the anions (−) towards the anode. Let us imagine the speed of the cations is higher than that of the anions and under the influence of an applied E.M.F. at a given time, while 4 cations move towards cathode, 2 anions move towards anode. This means that the cations would carry double the amount of current relative to the anions. This is shown in the second row of the figure. During this time 2 anions will leave the cathode compartment (C) and 2 anions will enter the anode compartment (A). Immediately 4 cations will leave the anode compartment (A).



− +
Cathode
C
B
A
Anode
6 Cations are liberated at the Cathode
6 anions are liberated at the anode

Fig. 9.6

After this migration it is clear that the concentration of the central compartment remains unaltered because the number of + *ve* and − *ve* ions which left this compartment is equal to the number of + *ve* and − *ve* ions entered here. The second row of the figure reveals that equivalent amount of cation and anion (6 each) will be discharged at the cathode and anode respectively to maintain neutrality of the electrolyte. The 3rd row of the figure shows that the concentration of the ions in the solution is different in cathode and anode due to difference in the speed of the ions. From the above it is apparent that the amount of electrolyte lost from each compartment is proportional to the speed of the ions migrating away from it and always equivalent quantities of different ions are liberated at the two electrodes in a given electrolyte in accordance with Faraday's second law of electrolysis despite of the difference in the speeds of the ions moving towards the respective electrodes.

9.6. Factors influencing electrolysis.

If an electrolyte contains only one species of cation and one species of anion as in molten NaCl then Na will be deposited at the cathode and Cl_2 at the anode but, if an electrolyte contains more than one species of cations and one species of anions then discharge of the particular species of cation or anion at the respective electrode depends upon several factors. Thus a dilute aqueous solution of NaCl contains four species of ions Na^+, H^+, OH^- and Cl^-. When this solution is electrolysed hydrogen gas is liberated in preference to metallic sodium and O_2 gas is liberated at anode but not Cl_2 gas. The term selective discharge denotes the preferential discharge/deposit of ions at respective electrodes. The control of this selective discharge depends upon various factors.

(1) Electronegative character of the ions : *As the electropositive character of the metals increases, the potential applied across the electrodes to discharge them will also increase.* In terms of electrode potential (see Vol II), elements with high negative electrode potential (reduction) will be least readily discharged at the cathode while metals with less negative electrode potential (reduction) will be more readily discharged at the cathode. Thus in a solution containing Zn^{++} and Na^+ ions, Zn will be preferentially deposited to sodium at the cathode [$E^\circ_{Zn^{++}/Zn} = -0.76$ volt and $E^\circ_{Na^+/Na} = -2{\cdot}71$ volt]. The change of $Zn^{++} + 2e \rightarrow Zn$ will occur more readily than the change of $Na^+ + e \rightarrow Na$. Similarly higher potential will be required for the discharge of sodium from NaCl than Cu from $CuSO_4$ because Na is more electropositive than Cu. ($E^\circ_{Cu^{++}/Cu} = 0.34$ volt). Thus in a mixture of NaCl and $CuCl_2$, Cu^{++} ion will be discharged more readily than Na^+ and even more readily than Zn^{++} ion.

The metals occurring at the lower part of the electrochemical series i.e., which are less electropositive, their cations have a higher tendency to be liberated at the cathode. On the other hand, metals which occur at the upper side of the electrochemical series i.e., which are strongly electropositive, the tendency of their cations to be discharged at the cathode is comparatively low. On the basis of this observation as well as discussion with reference to the electrochemical series a list of ions can be drawn indicating the order in which they are selectively discharged at the electrodes.

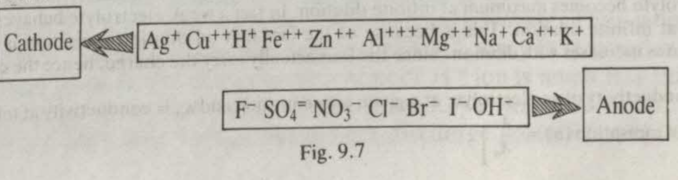

Cathode
Ag⁺ Cu⁺⁺ H⁺ Fe⁺⁺ Zn⁺⁺ Al⁺⁺⁺ Mg⁺⁺ Na⁺ Ca⁺⁺ K⁺
F⁻ SO₄⁼ NO₃⁻ Cl⁻ Br⁻ I⁻ OH⁻
Anode

Fig. 9.7

Or in other words, Ag^+ ion is preferentially discharged to Cu^{++} while Cu^{++} is preferentially deposited to H^+ at the Cathode. If we look to the anion then OH^- ion is preferentially discharged to Cl^- ion.

Thus when a very dilute aqueous solution of NaCl is electrolysed, hydrogen and oxygen gases are liberated at the cathode and anode respectively. The following ions are present in an aqueous solution of NaCl

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

H^+ ion is preferentially discharged to Na^+ at cathode and OH^- ion (giving rise to O_2 gas) is preferentially discharged to Cl^- ion at the anode (see fig 9.7) as Cl^- is more electronegative than OH^- and Na^+ is more electropositive than H^+.

(2) **Relative densities of the ion in solution :** The density of the electrolytic solution plays a significant role in predicting the ions migrated to the electrodes. Thus when a dilute solution of H_2SO_4 is electrolysed between Pt electrodes OH^- ion is preferentially discharged to SO_4^{--} at the anode since the concentration of OH^- ions is more than that of SO_4^{--}.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Anode reaction :

$$OH^- - e = OH$$
$$4OH = 2H_2O + O_2$$

Hence O_2 will be liberated at the anode. Hydrogen is liberated at the cathode.

If, on the other hand, the concentration of H_2SO_4 is increased, the density of SO_4^{--} is increased, the density of SO_4^{--} becomes more than that of OH^- ion. Hence passage of electric current through concentrated H_2SO_4 will cause the discharge of SO_4^{--} ion at the anode instead of OH^- ion. When 60% H_2SO_4 solution is electrolysed, perdisulphuric acid is formed at the anode not O_2 gas in accordance with the following equation.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

Anode reaction :

$$HSO_4^- - e = HSO_4$$
$$2HSO_4 = \underset{\text{perdisulphuric acid}}{H_2S_2O_8}$$

A mixture of two metallic ions can be discharged at the cathode in the form of alloy by carefully balancing their concentration in solution since, as already mentioned, an ion having lower concentration in solution is more difficult to discharge than the same ion at higher concentration. Thus when a mixture of $ZnSO_4$ and $CuSO_4$ with proper concentration is electrolysed, the alloy brass can be deposited at the cathode. Therefore whether an ion will be discharged or not at the electrode must depend upon its concentration in solution.

[It is true that conductivity of a solution increases with the dilution with water. The conductivity of a weak electrolyte becomes maximum at infinite dilution. In fact a weak electrolyte behaves like a strong electrolyte at infinite dilution. This is because of the fact that on dilution ionisation is more, so the number of ions increases with dilution. Since the ions actually carry the charge, hence the conductivity is increased.

If λ = conductivity of an electrolyte at a given concentration and λ_o = conductivity at infinite dilution the degree of ionisation $(\alpha) = \dfrac{\lambda}{\lambda_o}$]

(3) **Nature of the Electrodes :** The nature of the electrodes during electrolysis of a solution must be taken into account in predicting whether an ion is likely to be preferentially discharged to the other or not. Thus when an aqueous solution of sodium chloride is electrolysed using Pt electrode, hydrogen gas is evolved at the cathode. But if Hg electrode is used instead of Pt, metallic sodium is deposited on the cathode. Similarly use of Pt electrode in the electrolysis of $CuSO_4$ solution releases Cu^{++} ions at the cathode and OH^- ions at the anode. But if Cu electrode is used SO_4^{--} ions are discharged at the anode—not OH^- ions.

(4) **Effect of over voltage :** Another factor which must be taken into account in predicting the discharge of an ion is *over voltage*. We know the potential required to discharge a metallic ion at an electrode is equal to its electrode potential (reduction). But higher potential will be required than the electrode potential (reduction) for the discharge of gaseous materials from an electrolyte containing Cl^-, OH^- and H^+ ions. Over voltage is the difference between the experimental decomposition potential and the electrode potential. Over voltage depends upon the nature of electrode, particular ion and even upon the particular way in which electrolysis is carried out.

Some over voltage values are :—

Gases	Electrode	Over voltage
Hydrogen	Ag	0·15 volt
"	Zn	0·70 "
"	Hg	0·78 "
Oxygen	Pb	0·31 "
"	Au	0·53 "
Chlorine	Pt	0·70 "

An aqueous solution of $ZnSO_4$ contains the following two equilibria—

$$ZnSO_4 \rightleftharpoons Zn^{++} + SO_4^{--}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Now if electric current is passed through the above solution containing Pt electrode, hydrogen gas is evolved since hydrogen is said to have low over voltage at Pt electrodes. If Zn electrodes are however used, Zn^{++} ions will be selectively discharged at the cathode since hydrogen has high over voltage at Zn electrode.

(5) **Discharge potential :** The preferential discharge of an ion during electrolysis is also controlled by its *discharge potential (decomposition voltage) which is the minimum potential required to discharge or liberate an ion at the electrode.* The lower the discharge potential of an ion, the higher is the ease of its discharge or liberation at an electrode.

In fact *discharge potential is defined as the sum of electrode potential of the ion and over voltage.*

Discharge potential = Electrode potential + over voltage at the electrodes

Normally the over voltage of metallic ions is small hence in the discharge of a metal from an ion, electrode potential is the controlling factor. *As in over voltage, discharge potential also depends upon the nature of electrode.* Thus when electric current is passed through an aqueous solution of NaCl, using Pt electrodes hydrogen gas is evolved because the discharge potential of H^+ ion is much less than that of Na^+ ion in Pt electrode. But if Hg cathode is used, Na^+ ions will be discharged as hydrogen has a high over voltage hence high discharge potential at Hg electrode.

Of the fact that use of Pt electrode liberates oxygen at the anode but in Hg cathode and carbon anode Cl_2 gas is evolved in preference to O_2 gas since O_2 has a higher over voltage (hence higher discharge potential) than chlorine at the carbon anode.

9.7. Examples of Electrolysis.

Electrolysis of water : Pure water is a very poor conductor of electricity. This is because of the fact that water molecule dissociates into H^+ and OH^- ions to a negligible extent. However addition of a little acid increases the conductivity of water to a considerable extent.

[In fact water does not contain free H^+ ion. It combines with water to form H_3O^+ ion. Therefore, electrolysis of water should be represented as $2H_2O \rightleftharpoons H_3O^+ + OH^-$]

A glass vessel having two vertical platinum foils entered through the rubber cork that closes the bottom is half filled with water. A few drops of conc. H_2SO_4 is added to water to make it acidulated. Two graduated tubes filled with water are inverted over the Pt foils (Fig 9.8). The foils are now connected to the positive and negative terminals of a battery. Electric current sets in. It is observed that the bubbles of gases begin to evolve and collect in the two test tubes and the volume of hydrogen generated at the cathode will be double that of oxygen collected at the anode.

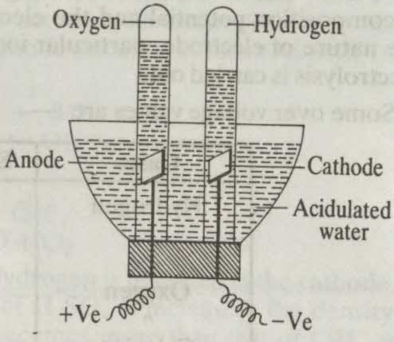


Fig 9.8 : Electrolysis of water

As a result of electrolysis H^+ ion migrates to the cathode, accepts electron and is neutralised to form hydrogen atom. Two hydrogen atoms then form molecular hydrogen. OH^- ion on the other hand migrates towards anode, releases electron to form OH radical that finally forms oxygen at the anode.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode

$H^+ + e = H$

$H + H = H_2 \uparrow$

At anode

$OH^- - e = OH$

$4OH = 2H_2O + O_2 \uparrow$

1. (a) Electrolysis of fused sodium chloride :

NaCl is a strong electrolyte. It exists as Na^+ and Cl^- ions. If electricity is passed through fused NaCl (as in Down's process for the manufacture of metallic sodium) using Pt cathode and graphite anode, Na is deposited on the cathode and Cl_2 is evolved at the anode according to the following simple mechanism :

NaCl ↓ Na^+ Cl^-

Na^+ discharged $\xleftarrow[\text{Cathode}]{\text{To}}$ Na^+ Cl^- $\xrightarrow[\text{Anode}]{\text{To}}$ Cl^- discharged

$Na^+ + e \rightleftharpoons Na \downarrow$ [Reduction]

$Cl^- - e \rightleftharpoons Cl$

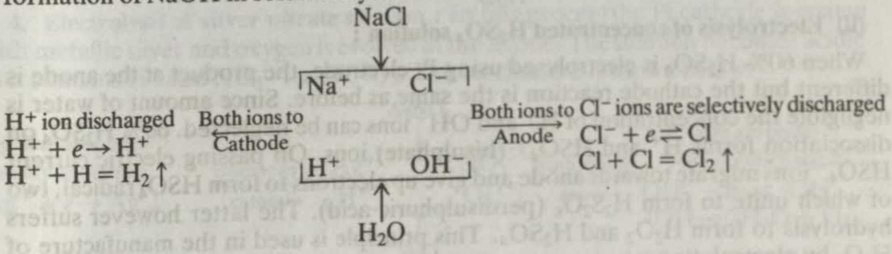
$Cl + Cl \rightleftharpoons Cl_2$ [Oxidation]

(b) Electrolysis of concentrated solution of sodium chloride :

A concentrated solution of NaCl contains Na^+ and Cl^- ions. Water also contains small quantities of H^+ and OH^- ions. Substantial amount of Na^+ and Cl^- ions are present in concentrated solution of NaCl.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

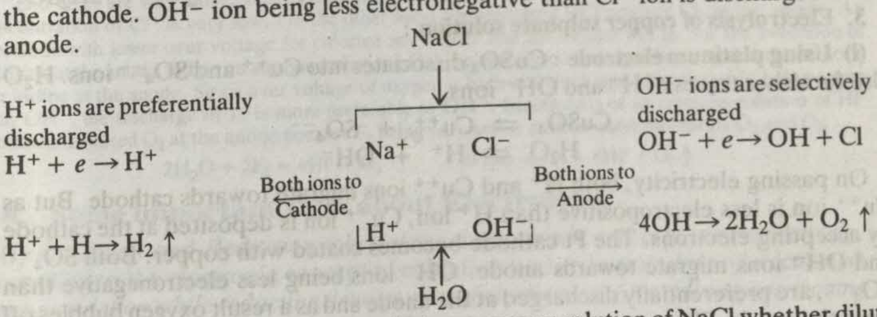
On passing electric current through Pt electrodes both Na^+ and H^+ ions migrate towards cathode while Cl^- and OH^- towards anode. Since H^+ is less electro-positive than Na^+, and has lower discharge potential than Na^+ ion, H^+ ion is preferentially discharged at the cathode as H_2 gas by accepting electron. Since OH^- ion is less electro-negative than Cl^- ion, it has more tendency to migrate towards anode and discharge in the form of O_2 gas. But the solution is highly concentrated, hence the concentration of Cl^- ion is more than that of OH^- ion. Again oxygen has a higher over voltage than chlorine at a graphite electrode. Hence Cl^- ions are selectively discharged at the anode instead of OH^- ions. As Na^+ ions are not discharged at the cathode, their concentration is increased around the cathode. OH^- ions also increase in concentration. The accumulation of both Na^+ and OH^- ions means the formation of NaOH in solution by the combination of Na^+ and OH^- ions.



$$Na^+ + OH^- \rightarrow NaOH$$

(c) Electrolysis of dilute NaCl solution :

A dilute aqueous solution of NaCl contains four ions Na^+, Cl^-, H^+ and OH^-. The electrolysis of dilute solution of NaCl yields hydrogen at the cathode and O_2 at the anode. As mentioned in the previous section H^+ ion is preferentially discharged at the cathode. OH^- ion being less electronegative than Cl^- ion is discharged at the anode.



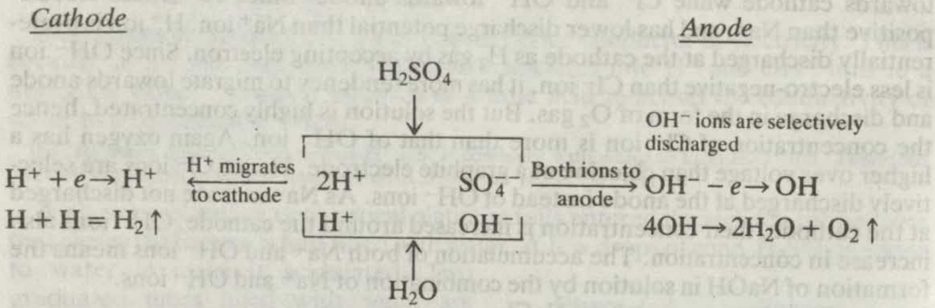
The above scheme demonstrates that an aqueous solution of NaCl whether dilute or concentrated never yields metallic sodium at the cathode.

2. (i) Electrolysis of dilute H_2SO_4 :

An dilute aqueous solution of H_2SO_4 contains H^+, SO_4^{--} and OH^- ions furnished by H_2SO_4 and H_2O.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

On passing electricity through Pt electrode hydrogen is liberated at the cathode through the process of reduction i.e., by taking up electron. Again OH^- is less electronegative than SO_4^{--} ion and the discharge potential of OH^- ion is less than that of SO_4^{--} ion, hence OH^- ion is discharged at the anode through the process of oxidation. Hence H_2 and O_2 are liberated at the cathode and anode respectively. This is, in fact, an example of electrolytic decomposition of water.


Cathode
Anode
H_2SO_4
OH⁻ ions are selectively discharged
$H^+ + e \rightarrow H^+$
H⁺ migrates to cathode
$2H^+$
SO_4^{--}
Both ions to anode
$OH^- - e \rightarrow OH$
$H + H = H_2\uparrow$
H^+
OH^-
$4OH \rightarrow 2H_2O + O_2\uparrow$
H_2O

(ii) Electrolysis of concentrated H_2SO_4 solution :

When 60% H_2SO_4 is electrolysed using Pt electrode, the product at the anode is different but the cathode reaction is the same as before. Since amount of water is negligible the concentration of H^+ and OH^- ions can be neglected. 60% H_2SO_4 on dissociation forms H^+ and HSO_4^- (bisulphate) ions. On passing electric current HSO_4^- ions migrate towards anode and give up electrons to form HSO_4 radical, two of which unite to form $H_2S_2O_8$ (perdisulphuric acid). The latter however suffers hydrolysis to form H_2O_2 and H_2SO_4. This principle is used in the manufacture of H_2O_2 by electrolytic process.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

At cathode

$$H^+ + e \rightarrow H$$
$$H + H \rightarrow H_2\uparrow$$

At anode

$$HSO_4^- - e \rightarrow HSO_4$$
$$HSO_4 + HSO_4 \rightarrow H_2S_2O_8$$
$$H_2S_2O_8 +. 2H_2O \rightarrow H_2O_2 + 2H_2SO$$

3. Electrolysis of copper sulphate solution :

(i) Using platinum electrode : $CuSO_4$ dissociates into Cu^{++} and SO_4^{--} ions. H_2O also furnishes traces of H^+ and OH^- ions.

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

On passing electricity, both H^+ and Cu^{++} ions migrate towards cathode. But as Cu^{++} ion is less electropositive than H^+ ion, Cu^{++} ion is deposited at the cathode by accepting electrons. The Pt cathode becomes coated with copper. Both SO_4^{--} and OH^- ions migrate towards anode. OH^- ions being less electronegative than SO_4^{--}, are preferentially discharged at the anode and as a result oxygen bubbles off from the anode. Thus on passing electricity Cu is deposited on the cathode, O_2 gas is evolved at the anode. H^+ and SO_4^{--} ions combine to form H_2SO_4. The resulting solution becomes highly acidic.

At cathode

$$Cu^{++} + 2e \rightleftharpoons Cu\downarrow$$
$$2H^+ + SO_4^{--} = H_2SO_4$$

At anode

$$OH^- - e = OH$$
$$4OH = 2H_2O + O_2\uparrow$$

(ii) Using copper electrodes :

Here copper is deposited on the cathode. The weight of copper cathode will increase. At the anode the following three processes may take place.

(a) $Cu - 2e \rightleftharpoons Cu^{++}$ (b) $SO_4^{--} - 2e \rightleftharpoons SO_4^{--}$

(c) $OH^- - e \rightleftharpoons OH$

In fact each copper atom of anode gives up two electrons and form Cu^{++} ion i.e., anode slowly dissolves and loses its weight. The rate of deposition of copper from $CuSO_4$ solution is the same as the rate of dissolution of copper anode into solution. Since the electrode potential $E^0_{Cu/Cu^{++}}$ and $E^0_{Cu^{++}/Cu}$ at the two electrodes are equal, there is really no decomposition taking place. Copper simply being transferred to cathode from the anode. The two weights being equal, the strength of the solution remains constant after electrolysis.

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

$$\underline{\text{At cathode}} \qquad\qquad \underline{\text{At anode}}$$

$$Cu^{++} + 2e \rightleftharpoons Cu\downarrow \qquad\qquad Cu - 2e \rightleftharpoons Cu^{++}$$

4. Electrolysis of silver nitrate solution : In this process the Pt cathode is coated with metallic silver and oxygen is evolved at the anode. The solution becomes acidic as it contains H^+ and NO_3^- i.e., HNO_3. The mechanism is shown below.

$$AgNO_3$$

$$\downarrow$$

Ag⁺ ions are preferentially discharged

$$Ag^+ + e \rightarrow Ag\downarrow \quad \xleftarrow[\text{cathode}]{\text{Both ions to}} \quad \begin{bmatrix} Ag^+ & NO_3^- \\ H^+ & OH^- \end{bmatrix} \quad \xrightarrow[\text{anode}]{\text{Both ions to}} \quad OH^- - e \rightleftharpoons OH$$

OH⁻ ions are preferentially discharged

$$4OH \rightarrow 2H_2O + O_2$$

$$\uparrow$$

$$H_2O$$

Resulting solution : $H^+ + NO_3^- \rightarrow HNO_3^-$

If Ag electrode is used, metallic silver is deposited on the cathode. The Ag anode goes into solution as Ag^+. The strength of the solution does not change.

[When hydrochloric acid solution is electrolysed, hydrogen is evolved at the cathode but either chlorine or oxygen at the anode, the evolution of which is governed by various factors. The discharge potential of Cl^- and OH^- are very close. When dilute HCl is electrolysed O_2 is evolved at the anode because the concentration of Cl^- is very low. On the other hand concentrated HCl produce Cl_2 at the anode. An electrode with lower over voltage for chlorine and higher one for oxygen will favour the evolution of chlorine at the anode. When an aqueous solution of HI is electrolysed hydrogen is evolved at the cathode but iodine at the anode. Since over voltage of oxygen is high and discharge potential of I^- being lower than OH^-, the discharge of I^- is more preferable to OH^-. Electrolysis of an aqueous solution of HF produces ozonised O_2 at the anode because F_2 being very active attacks water and forms O_2 and O_3.

$$2H_2O + 2F_2 = 4HF + O_2 \qquad 3H_2O + 3F_2 = 6HF + O_3.]$$

9.8. Some important facts about Electrolysis.

(i) *Oxidation and Reduction take place at the anode and cathode respectively.* According to the electronic concept of oxidation and reduction, *loss of electron(s) means oxidation while reduction denotes gain of electron(s). An oxidising agent gains electron(s) while a reducing agent loses electron(s).*

$$Ox + ne \rightleftharpoons Red$$

Ox = Oxidising agent

Red = Reducing agent

On passing electricity through the electrolyte cations migrate towards cathode, capture electron(s) and are reduced while the anions migrate towards the anode and give up electron(s) and thus oxidised. Hence cations are reduced while anions are oxidised. *Therefore, electrode reactions during electrolysis are redox reactions.*

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At cathode	*At anode*
$Na^+ + e \rightarrow Na$ [Reduction]	$Cl^- - e \rightleftharpoons Cl$ [Oxidation]
[$Ox + ne \rightleftharpoons Red$]	[$Red - ne \rightleftharpoons Ox$]

(ii) *Redox reaction takes place only at the electrodes.*

It is observed that only when electric current is passed through the electrolyte, the gain or loss of electron(s) by the ions takes place. The process stops as soon as passage of electricity is withdrawn.

(iii) *The number of electrons lost at the anode by the anion is the same as that gained at the cathode by the cation.*

(iv) The overall chemical reaction during electrolysis takes places through two half cell reactions at two electrodes. The cation is neutralised by reduction and the anion by oxidation at the two electrodes. The new products are formed as a result of the sum of the two reactions at the two electrodes.

(v) Electrons flow from cathode to anode through the electrolytes during electrolysis. Hence current flows in the opposite direction from anode to cathode through the electrolytes.

9.9. Practical units of electric current and quantity of electricity.

(A) **Coulomb** and **Faraday** are the two units of quantity of electricity. Coulomb is the practical unit while Faraday is the bigger unit of quantity of electricity.

(i) **Coulomb :** This unit is named after Charles de Coulomb (1736-1806), a french physicist. It is defined as *the quantity of electricity that liberates 0.001118 g of Ag at Pt cathode when current is passed through $AgNO_3$ solution or 0·0000104 g of hydrogen from dil. HCl solution. It is equal to the charge transferred by a current of one ampere in one second through any electrolyte.*

(ii) **Faraday :** *A Faraday is defined as the quantity of electricity that liberates or dissolves 1 gram-equivalent of any substance from an electrolyte at the electrode. Thus* when 1 Faraday of electricity is passed through an aqueous solution of $AgNO_3$, 108 g of Ag is deposited on the cathode. 108 is the equivalent weight of Ag.

$$\boxed{1 \text{ Faraday} = 96496 \text{ coulomb} \simeq 96500 \text{ coulmb}}$$

Thus when 96500 coulomb of electricity is passed through appropriate electrolytes 1.008 g of H_2, 35.5 g of Cl_2, 8 g of O_2 etc., are liberated at the electrodes. *It is the total charge of one mole of electrons.*

(B) **Ampere :** It is the practical unit of electric current and is named after A.M. Ampere (1775-1836). *It is defined as the current required to deposit 0.001118 g of Ag from a solution of silver nitrate in one second.*

Whenever 1 ampere current flows through an electrolyte for 1 second the total quantity of electricity will be 1 coulomb. If *c* ampere of current is passed for *t* second then the quantity of electricity $Q = c.t.$ or, coulomb = ampere × time (seconds) or Quantity of electricity (Q) = current (A) × time (t) (second).

9.10. Faraday's laws of electrolysis.

While studying the effect of electric current on chemical substances, Michael Faraday (1791-1867) observed that there is a quantitative relation between the quantity of electricity passing through an electrolyte and the amount of chemical changes occurring at the electrodes. The quantitative relations are known as

"Faraday's laws" which proved matter to be electrical in nature and showed equivalences between electrical energy and chemical changes.

(A) **Faraday's first law of electrolysis :**

The weight of a substance (expressed in gram) liberated or deposited at or dissolved from an electrode during electrolysis is directly proportional to the quantity of electricity passing through the electrolyte.

This implies that if the quantity of electricity is increased the weight of substance liberated or deposited will be increased. Similarly if less quantity of electricity is passed through the electrolyte then less amount of substance will be liberated at the electrode.

Let W g of a substance is deposited at the electrode due to the passage of Q coulomb of electricity through the electrolyte. According to the first law of Faraday :—

$$W \propto Q \text{ or, } \quad W = ZQ \; [Z \text{ is constant}]$$

Again $Q = C.t.$ where C is the current strength in ampere and t the time in seconds, we get $W = Zct$. Z is called Electrochemical equivalent (E.C.E) of a substance. The value of Z depends upon the nature of the substance.

- ***Definition of electrochemical equivalent :***

From first law we get $W = Z.c.t.$

Now if $C = 1$ ampere and $t = 1$ second i.e. $= 1$ coulomb

then $W = Z$

Thus the electrochemical equivalent of a substance is the weight in gram of that substance which is deposited or liberated at the electrode when 1 ampere current is passed through the electrolyte for 1 second or it is the weight, in gram of a substance liberated by 1 coulomb of electricity.

Thus when 1 coulomb of electricity is passed through $AgNO_3$ solution, 0.001118 g of Ag is deposited on the Pt cathode. Therefore, E.C.E of Ag = 0·001118 g/coulomb. E.C.E. of hydrogen = 0.0000104 g/coulomb ; Cu = 0.000329 g/coulomb.

- ***Relation between the mass of the substance and its E.C.E.***

When the same quantity of electricity is passed through different electrolytes, different amounts of the substances will be liberated at the electrodes. Let the same quantity of electricity say Q coulomb be passed through two different electrolytes, as a result of which W_1 *and* W_2 *g of two elements X* and Y are liberated at the two electrodes. Let Z_1 *and* Z_2 *be the E.C.E. of X and Y* respectively.

Applying first law :—

$$W_1 = Z_1, Q \quad \text{and} \quad W_2 = Z_2Q$$

$$\text{or, } \frac{W_1}{W_2} = \frac{Z_1}{Z_2} \quad \text{or, } W \propto Z$$

$$\text{or, } \frac{\text{The weight of } X \text{ in gram liberated at the electrode}}{\text{The weight of } Y \text{ in gram liberated at the electrode}} = \frac{\text{E.C.E. of } X}{\text{E.C.E. of } Y}$$

That is,

The weights of two elements in gram, deposited or liberated at the electrodes by the same quantity of electricity are directly proportional to their respective electrochemical equivalents.

If it is observed that if the same substance is liberated at the electrodes during the electrolysis of different electrolytes, then passage of 1 coulomb of electricity will cause the liberation of the same quantity of that substance inspite of the fact that the electrolytes are different. As for example when 1 coulomb of electricity is passed through acidulated water 0.0000104 g of H_2 will be liberated at the cathode. Similarly the passage of 1 coulomb of electricity through dil. solution of HCl will liberate the same amount of H_2 i.e., 0.0000104 g of H_2 at the cathode. If, on the other hand, different substances are liberated during the electrolysis of different electrolytes then different substances with variable weights will be liberated at the electrodes. Hence it may be said that E.C.E (Z) of a substance is constant but for different substances the values of E.C.E. are different.

Verification of First Law :

A known strength of current (C_1 ampere) is passed for a given time (say t seconds) through copper sulphate solution using Pt-electrode. The weight of copper deposited is noted (W_1 g). The current strength is changed (C_2, C_3, C_4 etc., ampere) and the weights of copper deposited (W_2, W_3, W_4 gram etc.,) are accurately measured. In every case, time of electrolysis remains constant.

Since $C_1 \times t = Q_1$, $C_2 \times t = Q_2$, $C_3 \times t = Q_3$ etc., it will be observed

$$\frac{W_1}{Q_1} = \frac{W_2}{Q_2} = \frac{W_3}{Q_3} \text{ (constant)}$$

or, $W \propto Q$ showing the validity of Faraday's first law of electrolysis. The results are recorded in a graph paper by plotting quantity of electricity Q_1, Q_2, Q_3 etc., against weights of copper deposited W_1, W_2, W_3, W_4 gram.

A straight line passing through the origin confirms the universility of the law,

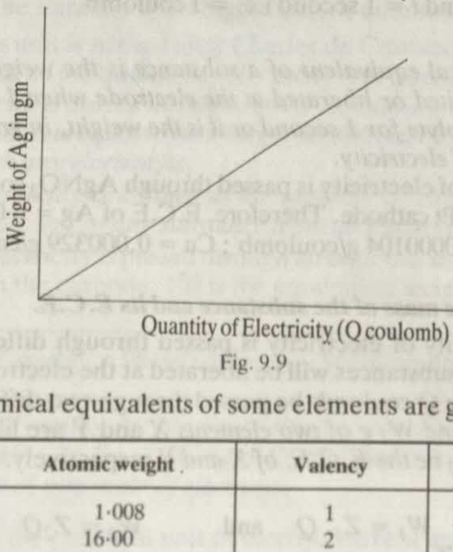


Fig. 9.9

The electro-chemical equivalents of some elements are given below :—

Element	Atomic weight	Valency	E.C.E. (gm/col)
Hydrogen	1·008	1	0·0000104
Oxygen	16·00	2	0·0000828
Chlorine	35·46	1	0·00036
Silver	107·88	1	0·001118
Magnesium	24·00	2	0·000126
Zinc	65·37	2	0·000339
Copper	63·54	1, 2	0·000329

(B) Faraday's second law of electrolysis :

When the same quantity of electricity is passed through solution of different electrolytes, the weights of different substances (in gram) liberated or deposited at or dissolved from the different electrodes are directly proportional to their respective chemical equivalents (equivalent weights).

The second law of Faraday implies that if the same quantity of electricity is allowed to pass through a number of cells, connected in series and containing different electrolytes in solution, then the relative weights of the elements liberated at the electrodes will be in the ratio of their respective equivalent weights.

Let W_1 g and W_2 g be the weights of two substances A and B respectively liberated at the two electrodes of two cells connected is series containing two different electrolytes due to passage of Q coulomb of electricity. Let E_1 and E_2 be the chemical equivalents or equivalent weights of A and B respectively.

According to Faraday's second law of electrolysis We get $W_1 \propto E_1$ and $W_2 \propto E_2$,

$$\therefore \quad \frac{W_1}{W_2} = \frac{E_1}{E_2}$$

$$\text{or,} \quad \frac{\text{Weight of } A \text{ deposited}}{\text{Weight of } B \text{ deposited}} = \frac{\text{Equivalent weight of } A}{\text{Equivalent weight of } B}$$

$$\text{i.e.,} \quad W \propto E$$

Thus when 1·008 g of hydrogen is liberated in one cell, 31·75 g of copper and 108 g of Ag will be liberated in other cells subject to one condition that same amount of electricity must be passed through the electrolytes.

Verification of Faraday's second law :

The validity of the second law of Faraday is proved by passing a definite amount of electricity for a constant period of time through three cells containing different electrolytes and measuring the weight of different substances liberated at the respective electrodes. Three cells are connected in series containing dil. H_2SO_4, $CuSO_4$ and $AgNO_3$ solution. A known constant current is passed through the electrolytes for a given period of time. After the time period the electrodes are weighed. It would be observed that when 1·008 g of hydrogen and 8 g of oxygen are evolved in the first cell, 31·75 g of copper and 108 g of Ag are deposited on the second and third cell respectively. Now 1·008, 8, 31·75 and 108 are the equivalent weights of hydrogen, oxygen, copper and silver respectively.

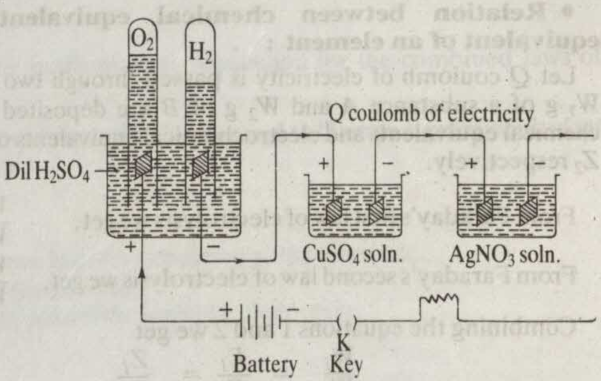


Fig. 9.10

- **Liberation of gm-equivalent amount of substance during electrolysis :**

We know that, *the quantity of electricity required to liberate, dissolve or deposit 1 gram-equivalent amount of any substance at the electrodes is called 1 Faraday.*

1 Faraday = 96500 coulombs. Since the charges carried by ions are different and the substances are liberated either by gain or loss of electrons, it is logical to conclude that the substances are deposited in the ratio of gram-equivalents and not in gram-atoms during electrolysis.

(i) *For monovalent ion :*

1 gram-equivalent of a monovalent atom is the same as its gram-atom and contains

Avogadro number ($6{\cdot}023 \times 10^{23}$) of atoms or ions. Monovalent ion requires 1 electron for neutralisation.

$$\begin{aligned} Ag^+ &+ e \rightarrow Ag \\ H^+ &+ e \rightarrow H \\ Li^+ &+ e \rightarrow Li \end{aligned}$$

Therefore, 1 Faraday of electricity or $6{\cdot}023 \times 10^{23}$ electrons are required to convert 1 gram-ion of a monovalent ion into 1 gram equivalent or 1 gram-atom.

[$6{\cdot}023 \times 10^{23}$ electrons carry 1 Faraday or 96500 coulomb of electricity.]

(ii) *For bivalent ions* (Cu^{++}, Mg^{++} or Ca^{++})

A bivalent cation will be neutralised by gaining two electrons.

$$\begin{aligned} Cu^{++} &+ 2e \rightarrow Cu \\ Mg^{++} &+ 2e \rightarrow Mg \end{aligned}$$

Therefore half the amount of 1 gram-ion or 1 gram-equivalent of a bivalent ion will be neutralised by $6{\cdot}023 \times 10^{23}$ electrons or 1 Faraday of electricity.

∴ 1/2 g ions of a bivalent ion = 1 gm-equivalent of bivalent ion. This amount will be liberated at the electrode during electrolysis.

(iii) *For trivalent ion* (Al^{+++}, Fe^{+++}, Cr^{+++})

1 Faraday or $6{\cdot}023 \times 10^{23}$ electrons will neutralise 1/3 gram-ion of a trivalent ion or 1 gram-equivalent of trivalent ion. Same explanation is applicable to negative ions or anions.

- **Relation between chemical equivalent and electrochemical equivalent of an element :**

Let Q coulomb of electricity is passed through two different electrolytes when W_1 g of a substance A and W_2 g of B are deposited on the electrodes. Let the chemical equivalents and electrochemical equivalents or A and B are E_1, E_2 and Z_1, Z_2 respectively.

From Faraday's first law of electrolysis we get, $\dfrac{W_1}{W_2} = \dfrac{Z_1}{Z_2}$ .... (1)

From Faraday's second law of electrolysis we get, $\dfrac{W_1}{W_2} = \dfrac{E_1}{E_2}$ .... (2)

Combining the equations 1 and 2 we get

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}$$

$$\text{or, } \frac{E_1}{E_2} = \frac{Z_1}{Z_2} \text{ or, } E \propto Z$$

$$\text{or, } \frac{\text{Weight of } A \text{ in gram}}{\text{Weight of } B \text{ in gram}} = \frac{\text{C.E. of } A}{\text{C.E. of } B} = \frac{\text{E.C.E. of } A}{\text{E.C.E. of } B}$$

or, *The chemical equivalent of a substance is directly proportional to its electrochemical equivalent.*

Let one of the substance be hydrogen :

E.C.E. of hydrogen = 0.0000104 g/coulomb and its C.E. = 1.008

$$\therefore \frac{E_1}{1.008} = \frac{Z_1}{0.0000104}$$

$$\text{or, } Z_1 = \frac{E_1 \times 0.0000104}{1.008}$$

$$\therefore \text{E.C.E. of an element} = \frac{\text{Its chemical equivalent} \times 0.0000104}{1.008}$$

When chemical equivalent of hydrogen is taken as 1 then,
E.C.E. of an element ≈ Its C.E. × 0.0000104
or, *E.C.E. of an element = Its C.E. × E.C.E. of hydrogen.*

- **Combination of first and second law of electrolysis :**

Let E = Chemical equivalent of a substance.
W = Weight of the substance deposited in gram.
Q = Quantity of electricity in coulomb passed through the electrolyte.

From first law :—

$$W \propto Q \qquad \text{when } E \text{ is constant}$$

From second law :—

$$W \propto E \qquad \text{when } Q \text{ is constant}$$

$$\text{or, } W \propto Q.E \qquad \text{when both } Q \text{ and } E \text{ vary}$$

$$\text{or, } W = K.Q.E \qquad K = \text{constant}$$

Experimentally K is found to be $1/F$ where $F = 1$ Faraday or 96500 coulomb.

$$\therefore W = \frac{Q.E}{F}$$

Since $Q = c.t.$ c = current in ampere, t = time in seconds

$$\therefore W = \frac{E.c.t}{F}$$

$$\text{or, } W = \frac{E.c.t}{96500}$$

The above equation is the mathematical expression for the combined laws of electrolysis.

- **To prove that 1 Faraday of electricity is required to liberate 1 gram equivalent of a substance at the electrode :**

We know, $W = \dfrac{QE}{F}$

W = Weight of the substance in gram deposited at the electrode.
E = Equivalent weight of the substance.
Q = Quantity of electricity passed through the electrolyte.

$$\text{or, } Q = \frac{W}{E} \times F$$

If 1 gram equivalent of a substance is liberated by the passage of Q coulomb of electricity then $W = E$.

$$\text{or, } Q = \frac{E}{E} \times F$$

$$\text{or, } Q = F$$

i.e., 1 Faraday or 96500 coulomb of electricity will be required for the liberation of 1 gram equivalent of a substance at the electrode.

- **Numerical value of F :**

We know that E.C.E. of hydrogen and silver are 0.0000104 g/col and 0.001118 g/col respectively. The equivalent weight of H = 1.008 and that of Ag = 107.88

Now,
0.0000104 g of hydrogen is liberated by 1 coulomb of electricity.

$\therefore$ 1.008 g of hydrogen is liberated by $\dfrac{1 \times 1.008}{0.0000104}$

= 96500 coulombs (approx.)

Again,

0.001118 g of silver is deposited by 1 coulomb of electricity

$\therefore$ 107.88 g of silver is deposited by $\frac{1 \times 107.88}{0.001118} = 96500$ coulomb (approx.)

Thus it is seen that 96500 coulomb of electricity are required to liberate 1 gram equivalent or 107.88 g of Ag or 1.008 g of hydrogen. This is the quantity of electricity required to liberate 1 gram equivalent of any other element. It is used as a distinct unit known as Faraday i.e., 1 Faraday = 96500 coulomb.

Thus when 1 Faraday or 96500 coulomb of electricity is passed through fused NaCl, 23 g of sodium will be deposited at the cathode and 35.5 g of chlorine gas or $\frac{1}{2} \times 22.4 = 11.2$ litre of chlorine gas will be evolved at the anode.

- **Relation between Faraday and E.C.E. of any element :**

From first law we get, $W = ZQ$

Again $W = \frac{Q.E}{F}$

Putting the value of W in the second equation,

$$ZQ = \frac{Q.E}{F} \quad \text{or, } Z = \frac{E}{F}$$

$$\text{E.C.E of an element} = \frac{\text{Its C.E.}}{F}$$

$$\text{or, } 1 \text{ Faraday} = \frac{\text{C.E. of an element}}{\text{E.C.E. of the element}}$$

Since the numerical value of F is constant, hence the ratio of C.E. and E.C.E of an element is always constant.

Again $E = F \times Z$ or, $E = 96500 \times Z$

or, ***Chemical Equivalent of an element = 96500 × Its electrochemical equivalent.***

9.11. Charge of 1 gram-ion = 1 Faraday.

Gram-ion : Ions are formed when atoms or radicals give up or gain electron (s). The mass of electron is negligible. So the mass of atoms or radicals may be taken as a mass of ions. Mass of atoms or radicals (O = 16.0000), when expressed in gram denotes gram of ions e.g.,

Atomic weight of Na = 23

$\therefore$ Gram ion of $Na^+ = 23$ g = 1 gram-ion of Na^+

The number of ions in 1 gram-ion is fixed. It is called Avogadro number. Its value is 6.023×10^{23}.

From First law of Faraday,

$W \propto Q$ when E is constant

From Second law,

$W \propto E$ when Q is constant

Combining the first and second laws we get, $W = \frac{Q.E.}{F}$

When 1 gram-equivalent of an element is deposited at the electrode, $W = E$ or, $F = Q$

Hence 1 Faraday or 96500 coulomb of electricity is required to liberate, deposit or dissolve 1 gram-equivalent of any substance i.e., 1 gram-equivalent ion carries 1 Faraday of electricity. Again it can be said that,

1 Faraday = 1 mole electronic charge = charge of 1 gram ion of a monovalent atom.

9.12. Relation among Faraday, Avogadro number and the charge of an electron.

The term electron was first employed by Stoney who used it for the unit charge on a monovalent negative ion. Faraday's laws of electrolysis showed matter to be electrical in nature and electricity consists of electrons. A relation among Faraday, Avogadro number and the charge of an electron can be deduced from a knowledge of Faraday's laws of electrolysis.

We know that *1 gram-equivalent of an ion carries one Faraday or 96500 coulomb of electricity.*

Again, 1 gram ion implies 1 gram atom of the element.

1 gram atom of an element = 1 gram-equivalent × valency.

∴ Charge of 1 gram ion = Charge of 1 gram-equivalent × valency

But charge of 1 gram-equivalent = 1 Faraday

∴ Charge of 1 gram ion = 1 Faraday × valency

If the valency of an ion is equal to n (a whole number) then :

Charge carried by 1 gram ion of an ion $= n \times F$.

Again, number of ions in 1 gram ion $= 6.023 \times 10^{23} = N$ (Avogadro number)

∴ The charge carried by (N) number of ions $= n \times F$.

Charge carried by a single ion with valency $n = n \times \left(\frac{F}{N}\right)$

∴ Charge carried by a single univalent ion $= 1 \times \left(\frac{F}{N}\right)$

∴ Charge carried by a single bivalent ion $= 2 \times \left(\frac{F}{N}\right)$

∴ Charge carried by a single trivalent ion $= 3 \times \left(\frac{F}{N}\right)$

Hence we can conclude that the quantity of electricity carried by an ion is either $\frac{F}{N}$ or simple multiples of $\frac{F}{N}$.

Therefore, $\left(\frac{F}{N}\right)$ *is the fundamental unit of charge.*

$$\therefore \text{The unit of electricity} = \frac{F}{N} = \frac{96500}{6.023 \times 10^{23}} \text{ coulomb}$$
$$= 1.602 \times 10^{-19} \text{ coulmbs}$$

As the *fundamental unit of negative charge is electron*

The charge of a single electron $e = \frac{F}{N} = 1.602 \times 10^{-19}$ coulomb.

- **Atomic nature of Electricity :**

The fundamental constituent of matter is atom. Similarly $\left(\frac{F}{N}\right)$ is regarded as the fundamental unit of electricity or fundamental unit of charge. Hence nature of electricity is also atomic like that of matter. This fundamental unit may be called 1 atomic electricity.

- **Charge of an electron :**

Charge of 1 gram ion of an univalent ion = 1 F = 96500 coulomb.

Again an univalent cation gains 1 electron and is neutralised at the cathode. Similarly an univalent anion loses 1 electron and is neutralised at the anode.

Let the charge of an electron be e

$\therefore$ Charge of univalent 1 gram ion $= N \times e = F$

(Number of univalent ions in 1 gram ion $= N$)

$$\therefore \; e = \frac{F}{N}$$

$$\text{or, } e = \frac{96500}{6.023 \times 10^{23}} \text{ coulomb } = 1.602 \times 10^{-19} \text{ coulomb.}$$

Hence the charge carried by 6.023×10^{23} or 1 mole of electron is 96500 coulomb.

On the basis of the above we can argue that *when 96500 coulomb of electricity is passed through an electrolyte or through a point of a metallic conductor, 6.023×10^{23} electrons are transported through the electrolyte or through the point of the conductor.*

Thus the number of electrons transported along the cross section of a metallic conductor $= \dfrac{F}{e} = \dfrac{\text{Quantity of electricity passing through the point}}{\text{Charge associated with an electron.}}$

- **Determination of Avogadro number :**

From his classical oil drop experiment Millikan showed that the charge of an electron is $1{\cdot}602 \times 10^{-19}$ coulomb.

$$\therefore \text{ Avogadro number } N = \frac{F}{e} = \frac{96500 \text{ coulomb}}{1.602 \times 10^{-19} \text{ coulomb}} = 6{\cdot}023 \times 10^{23}$$

Thus, knowledge of electronic charge and the value of Faraday helps us to find the numerical magnitude of N or Avogadro number.

Charge of an ion :

Charge carried by various ions of different valency can be evaluated with the help of the relation $e = F/N$.

A hydrogen ion is formed by the loss of an electron $H - e \rightarrow H^+$

$$\text{The charge carried by one } H^+ \text{ ion} = \frac{96500}{6{\cdot}023 \times 10^{23}} \text{ coulomb} = 1{\cdot}602 \times 10^{-19} \text{ coulomb.}$$

This is the unit of positive electricity.

The above is also the charge of an electron. Hence the charge carried by an electron is the same as that of a H^+ ion (proton) but it is of opposite nature.

The nature and quantities of electricity carried by some common ions are tabulated below.

Ions	Valency of Ions	Quantity of electricity $= n \times \frac{F}{N}$ coulomb	Nature of Charge
$H^+, Ag^+, K^+, Na^+, NH_4^+$	1	$1 \times 1.602 \times 10^{-19}$ coulomb	Positive
OH^-, Cl^-, NO_3^-, F^-	1	$1 \times 1.602 \times 10^{-19}$ coulomb	Negative
$Ca^{++}, Zn^{++}, Cu^{++}$ Mg^{++}, Sr^{++}	2	$2 \times 1.602 \times 10^{-19}$ $= 3.204 \times 10^{-19}$ coulomb	Positive
$S^{--}, SO_4^{--}, CO_3^{--}, SO_3^{--}$	2	$2 \times 1.602 \times 10^{-19}$ $= 3.204 \times 10^{-19}$ coulomb	Negative
$Al^{+++}, Fe^{+++}, Cr^{+++}$	3	$3 \times 1.602 \times 10^{-19}$ $= 4.806 \times 10^{-19}$ coulomb	Positive
$PO_4^{---}, N^{---}, P^{---}$	3	$3 \times 1.602 \times 10^{-19}$ $= 4.806 \times 10^{-19}$ coulomb	Negative

• Distinction between chemical equivalent (C.E.) and Electro chemical equivalent (E.C.E) of an element :

Electro chemical equivalent	Chemical equivalent
1. E.C.E. is the quantity of substance in gram formed at an electrode when 1 coulomb of electricity is passed through the electrolyte.	1. Chemical equivalent is a number which shows how many parts by weight of the element combine with or replace from a compound 1·008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weights of Cl_2.
2. Unit of E.C.E. of an element is gram coulomb^{-1}	2. It, being a ratio has no unit. It is a pure number.
3. The term E.C.E. is associated with the reaction taking place at the electrodes during electrolysis.	3. It is applicable to all types of reactions.
4. The numerical value of E.C.E. of an element very low.	4. The numerical value of C.E. of an element is comparatively higher than that of its E.C.E. C.E = Its E.C.E × 96500
5. E.C.E. of an element = Its C.E. × E.C.E. of hydrogen.	5. C.E. of an element is proportional to its E.C.E.

9.13. Practical applications of electrolysis.

The process of electrolysis finds its wide applications in various fields, some of the widely used applications are discussed here :

(1) **Electroplating :** In order to protect articles made of copper, iron, aluminium etc., against corrosion due to moisture and oxygen of air, superior metals like gold, silver, chromium, nickel etc., are deposited on them by the process of electrolysis. This art of deposition of metals in a finely divided state is called electroplating. Besides protection, electroplating enhances better looking and helps in repairing the irregular broken portion on the metals. Car bumpers are protected against corrosion by electroplating the steel with a coat of nickel and then a fine coat of chromium.

The metallic salts exist in the ionic state in aqueous medium. On passing electric current through such solutions the metallic ions i.e., cations migate towards the cathode, accept electrons and are deposited on the cathode as metal. If this metal is used as anode, the anodic metal dissolves in the electrolyte, migrates towards the cathode and is deposited there. As a result, a deposition of metal in the finely divided state occurs on the cathode.

An aqueous solution of $ZnSO_4$ dissociates as follows :—

$$ZnSO_4 \rightleftharpoons Zn^{++} + SO_4^{--}$$

On passing electricity Zn will be deposited on the cathode and SO_4^{--} ions migrate towards anode and react with zinc anode to form soluble $ZnSO_4$.

$$Zn^{++} + SO_4^{--} \rightleftharpoons ZnSO_4$$

If the metallic anodic ion is insoluble in the solution of the metal salt, the metallic ion will not be formed in solution. In that case, the metal salt solution is periodically added in order to increase the concentration of metallic ions in solution. The following points are taken into consideration in electroplating.

(a) The concentration of the metallic ion must be high.

(b) The electrolyte must be cheap, highly soluble and good conductor.

(c) The plating of the metal must be uniform.

(d) The metallic salt must be stable and unaffected by oxidation, reduction, hydrolysis.

(e) If the electrolyte is not a good conductor, the conductivity of the solution must be enhanced by the addition of salt of higher conductivity.

(f) Low temperature and high current density.

Procedure : The article to be electroplated is thoroughly rubbed with sand paper, washed with NaOH, acid and finally with distilled water. This is used as negative electrode (cathode) i.e., the spoon in Fig. 9.11. The metal to be deposited on the spoon is used as the anode. A soluble metal salt is used as an electrolyte. Electroplating is carried out in a tank made of wood, glass or cement. On passing a uniform electric current through a considerable length of time, the anodic material dissolves slowly and is deposited on the article. Finally the electroplated article is washed with water and dried in air.

Examples :

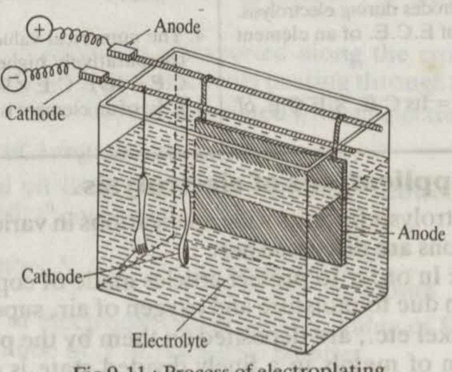


Fig 9.11 : Process of electroplating

(i) *Silver plating :* Here Ag anode is used and the electrolyte is K [Ag (CN)$_2$], potassium dicyano argenate (I) solution .

$$Ag^+ + e \rightarrow Ag$$

(ii) *Nickel plating* : Nickel as anode and $NiSO_4$ solution containing a trace of boric acid is used as electrolyte.

(iii) *Copper plating :* Copper plate as anode, $CuSO_4$ solution mixed with dilute H_2SO_4 as electrolyte.

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

$$\text{Cathode : } Cu^{++} + 2e \rightarrow Cu \downarrow$$

(iv) *Gold plating :* Pure gold plate as anode. The electrolyte is potassium dicyano aurate (I) K [Au(CN)$_2$].

(v) *Chromium plating :* Pure chromium plate as anode. A mixture of chromic sulphate and chromic acid as electrolyte.

(2) **Extraction metals :** Highly electropositive metals cannot be extracted by carbon reduction or self reduction process. They are obtained by the electrolysis of fused metallic chloride or hydroxide using suitable electrodes. Metals like Na, K, Ca, Mg, Al etc., are extracted by electrolytic method.

(3) **Refining of metals :** 99.9% pure metal is obtained by electro refining process. The impure metal is used as anode and the pure metal is used as cathode. The electrolyte is a soluble salt of the metal. On passing electric current impure metal at the anode dissolves and is deposited on the cathode. The impurities, called *anode mud* sinks to the bottom of the electrolyte and is recovered.

(4) **Preparation of chemicals :** Important chemicals like chlorine, HCl, NaOH, Na_2CO_3, $KClO_3$ etc., are manufactured by electrolytic process

(5) **Electrotyping :** It is an art of reproducing the form of an object say type (wood carving) by electro deposition on a block of wax from which it can be transferred

later. The wax is coated with graphite. It is used as the cathode, A copper anode is used and $CuSO_4$, dil H_2SO_4 are used as electrolyte. On passing electric current Cu is deposited on the way impression taken earlier. Wax is melted and is removed, Electrotyping is used for large scale printing purpose.

(6) **Electrochemical analysis :** Separation and quantitative estimation of metals by the application of electric current from a solution containing more than 1 metal ions constitute what is called electrochemical separation. Electrolytic separation of metals requires use of e.m.f. greater than the decomposition voltage of the salt under electrolysis. Electrolyte contains different metal ions having wide differences in decomposition voltage can be isolated from the solution and determined quantitatively one after the other. The process is called *Electrogravimetry* which consists in the deposition of the metal on a weighed electrode by electrolysis. Copper is determined electrogravimetrically from a solution of $CuSO_4$. Cu and Ni can be quantitatively separated from a mixture of $CuSO_4$ and $NiSO_4$.

- **Determination of equivalent weight :**

(7) *Equivalent weight of silver :* Two voltameters, one containing $AgNO_3$ and the other $CuSO_4$ solution having Ag and Cu electrodes respectively are connected in series with the battery and an ammeter. A rhehostate is inserted in the circuit. The two electrodes are cleaned, dried and weighed. On passing electric current through the circuit metallic Ag and Cu are deposited on the cathodes of respective voltameter. After electrolysis the cathodes are washed with water followed by alcohol, dried and weighed (Fig 9.12).

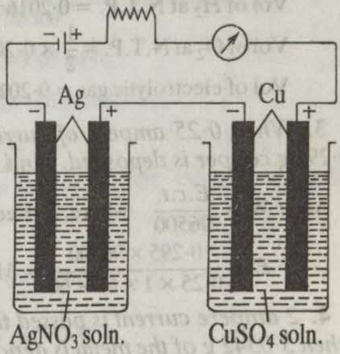


Fig 9.12 : Determination of chemical equivalent with the help of electrolysis

Calculations :

Weight of Cu cathode before electrolysis = w g
Weight of Cu cathode after electrolysis = w_1 g
Weight of copper deposited = $(w_1 - w)$ g
Weight of Ag cathode before electrolysis = w_2 g
Weight of Ag cathode after electrolysis = w_3 g
Weight of Ag deposited = $(w_3 - w_2)$ g

Let the equivalent weights of Ag and Cu be E_{Ag} and E_{Cu}

$$\therefore \frac{(w_1 - w)}{(w_3 - w_2)} = \frac{E_{Cu}}{E_{Ag}}; \quad E_{Cu} = 31.75 \text{ is known}$$

Hence E_{Ag} can be easily found out. The experimental value of Eq. wt. of Ag = 107.88.

9.14. Numerical Problems.

1. *2.5 amperes of current is passed through $CuSO_4$ solution for 30 minutes. Calculate the weight of copper in the cathode. Find the number of copper atoms.* *[Cu = 63.54]*

Ans : Eq. wt. of Cu = $\frac{63.54}{2} = 31.77$

$$w = \frac{E.c.t.}{F} = \frac{31.77 \times 2.5 \times 30 \times 60}{96500} = 1.4815 \text{ g}$$

1 gram atom of Cu i.e., 63.54 g of Cu contains 6.023×10^{23} atoms

$$\therefore \ 1.4815 \text{ g of Cu contains } \frac{6.023 \times 10^{23} \times 1.4815}{63.54}$$

$$= 1.404 \times 10^{22} \text{ copper atoms.}$$

2. *1·93 ampere of current is passed through dil. H_2SO_4 for 15 minutes. Calculate (i) weight of H_2, (ii) number of gram-mole of hydrogen, (iii) volume of hydrogen at N.T.P., (iv) number of hydrogen molecules, (v) volume of electrolytic gases at N.T.P.*

Ans : Quantity of electricity $= 1{\cdot}93 \times 15 \times 60 = 1737$ coulomb

(i) 96500 coulomb liberate 1 g of hydrogen

$$1737 \quad " \quad " \quad \frac{1 \times 1737}{96500} = 0{\cdot}018 \text{ g of hydrogen}$$

Weight of hydrogen $= 0{\cdot}018$ g

(ii) 1 gram-mole $H_2 = 2{\cdot}0$ g of H_2

$$\therefore \text{ Number of gram-mole} = \frac{0{\cdot}018}{2} = 0{\cdot}009 \text{ gram-mole.}$$

(iii) Vol of 2 g of hydrogen at N.T.P. $= 22{\cdot}4$ litre

$$\text{Vol of } 0{\cdot}018 \text{ g of hydrogen at N.T.P. } \frac{22{\cdot}4 \times 0{\cdot}018}{2} = 0{\cdot}2016 \text{ litre}$$

(iv) 1 gram-mole of hydrogen contains $6{\cdot}023 \times 10^{23}$ molecules

$0{\cdot}009$ gram-mole hydrogen contains $0{\cdot}009 \times 6{\cdot}023 \times 10^{23}$

$= 5{\cdot}42 \times 10^{21}$ molecules of hydrogen

(v) Volume Ratio of H : O = 2 : 1, when dil. H_2SO_4 is electrolysed

This gas mixture is called electrolytic gas

Vol of H_2 at N.T.P. $= 0{\cdot}2016$ litre.

$$\text{Vol of } O_2 \text{ at N.T.P.} = \frac{1}{2} \times 0{\cdot}2016 \text{ litre} = 0{\cdot}1008 \text{ litre}$$

Vol of electrolytic gas $= 0{\cdot}2016 + 0{\cdot}1008 = 0{\cdot}3024$ lt.

3. *When 0·25 ampere of current is passed through $CuSO_4$ solution for 1 hour, 0·295 g copper is deposited. Find the Eq. wt. of copper.*

$$\textbf{Ans : } W = \frac{E.c.t.}{96500} \quad \text{where, } E = \text{eq. wt. of copper} \quad \text{or, } 0{\cdot}295 = \frac{E \times 0{\cdot}25 \times 1 \times 60 \times 60}{96500}$$

$$E = \frac{0{\cdot}295 \times 96500}{0{\cdot}25 \times 1 \times 60 \times 60} = 31{\cdot}63$$

4. *2 ampere current is passed through a metal (M) chloride for 1 hour 15 minutes when 3·0342 g of the metal is deposited at the cathode. If the specific heat of the metal be 0·096, calculate exact at. wt. of the metal and the formula of the metal chloride.*

Ans : Quantity of electricity $= 2 \times (1 \times 60 + 15) \times 60 = 9000$ coulomb.

$$W = \frac{E.Q}{96500} \quad \text{or, } 3{\cdot}0342 = \frac{E \times 9000}{96500}$$

$$\text{or, } E = \frac{3{\cdot}0342 \times 96500}{9000} = 32{\cdot}53$$

$$\text{According to Dulong and Petit's law, the approx at. wt. of the metal (M)} = \frac{6{\cdot}4}{0{\cdot}096} = 66{\cdot}66$$

$$\text{Valency of the metal} = \frac{\text{At. wt.}}{\text{Eq. wt.}} = \frac{66{\cdot}66}{32{\cdot}53} \approx 2$$

Correct at. wt. of the metal $= 32{\cdot}53 \times 2 = 65{\cdot}06$

Formula of the chloride $= MCl_2$

5. *Calculate the number of electrons having charge of 1 coulomb.*

$$\textbf{Ans : } \text{Charge of 1 electron} = \frac{F}{N} = \frac{96500}{6{\cdot}023 \times 10^{23}} = 1{\cdot}602 \times 10^{-19} \text{ coulomb.}$$

$1{\cdot}602 \times 10^{-19}$ coulomb of electricity is contained in 1 electron

$$1 \text{ coulomb of electricity is contained in } \frac{1}{1{\cdot}602 \times 10^{-19}} = 6{\cdot}24 \times 10^{18} \text{ electrons.}$$

6. *How many electrons will be flown when 1 ampere of current is passed through dil. HCl solution for 1 seconds.*

Ans : $HCl \rightleftharpoons H^+ + Cl^-$

At cathode : $H^+ + e \rightleftharpoons H \qquad H + H = H_2\uparrow$

∴ Number of H^+ ion liberated at the cathode = Number of electrons captured.

Quantity of electricity = 1 × 1 = 1 coulomb.

1 gram-equivalent of H^+ contains $6{\cdot}023 \times 10^{23}$ H^+ ions

96500 coulomb of electricity discharge $6{\cdot}023 \times 10^{23}$ H^+ ions

$$\text{1 coulomb of electricity discharges } \frac{6{\cdot}023 \times 10^{23}}{96500} = 6{\cdot}24 \times 10^{18}\ H^+ \text{ ions.}$$

∴ Number of electron flown = $6{\cdot}24 \times 10^{18}$.

7. *0·965 ampere current is passed through 100 ml of 0·1(M) $CuSO_4$ solution for 1 minute. The reactions at the electrodes are—*

At cathode : $Cu^{++} + 2e \rightarrow Cu\downarrow$ *At anode :* $2H_2O \rightarrow O_2 + 4H^+ + 4e$

Calculate the molar concentration of Cu^{++}, H^+ and SO_4^{--} ions assuming volume of the solution does not change.

Ans : $W = \dfrac{E.c.t}{96500}$

$$W = \text{weight of Cu or Cu}^{++}\text{ ions deposited} = \frac{31{\cdot}75 \times 0{\cdot}965 \times 60}{96500} = 0{\cdot}01905 \text{ gram}$$

$$\text{Number of moles of Cu or Cu}^{++}\text{ ion} = \frac{0{\cdot}01905}{63{\cdot}5} = 0{\cdot}0003 \text{ mole.}$$

(i) *Before electrolysis,* number of moles of Cu^{++} ion in 100 ml solution

$$= \frac{0{\cdot}1 \times 100}{1000} = 0{\cdot}01$$

∴ *After electrolysis,* Number of moles of Cu^{++} ion in solution = 0·01 − 0·0003 = 0·0097

After electrolysis :

100 ml of $CuSO_4$ contain 0·0097 moles of Cu^{++}

$$\text{1000 ml of } CuSO_4 \text{ contain } \frac{0{\cdot}0097 \times 1000}{100} = 0{\cdot}097 \text{ mole/litre.}$$

$$\text{(ii) Weight of } H_2 \text{ during electrolysis} = \frac{1 \times 0{\cdot}965 \times 60}{96500} = 0{\cdot}0006 \text{ g}$$

$$\text{Number of moles of } H^+ \text{ ion} = \frac{0{\cdot}0006}{1} = 0{\cdot}0006 \text{ mole.}$$

Since, before electrolysis, the solution does not contain H^+ ion, 100 ml of the solution contains 0·0006 moles of H^+ ion after electrolysis.

$$\therefore \text{ Concentration of } H^+ \text{ ion in 1000 ml solution} = \frac{0{\cdot}0006 \times 1000}{100} = 0{\cdot}006 \text{ moles/litre.}$$

(iii) During electrolysis the concentration of SO_4^{--} ion does not change.

Hence the concentration of SO_4^{--} ion = 0·1 mole/litre.

8. *2 ampere of current is passed through 100 ml of 0·5 (N) $CuSO_4$ solution for some time. After electrolysis the concentration of the resulting solution becomes 0·1 (N). Find the time of passing electric current.*

Ans : *Before electrolysis :*

$$\text{Weight of Cu}^{++}\text{ ion} = \frac{0{\cdot}5 \times 31{\cdot}75 \times 100}{1000} = 1{\cdot}5875 \text{ g}$$

After electrolysis :

$$\text{Weight of Cu}^{++}\text{ ion} = \frac{0{\cdot}1 \times 31{\cdot}75 \times 100}{1000} = 0{\cdot}3175 \text{ g}$$

Weight of Cu^{++} ion liberated due to electrolysis

= 1·5875 − 0·3175 = 1·2700 g

Applying the equation $W = \frac{E.c.t.}{96500}$ $W = 1{\cdot}2700$ g $c = 2$ ampere $E = 31{\cdot}75$ g $t = ?$

$$t = \frac{1{\cdot}27 \times 96500}{31{\cdot}75 \times 2} = 1930 \text{ second.}$$

9. *10 g of a fairly concentrated solution of $CuSO_4$ is electrolysed using 0·01 Faraday of electricity. Calculate (i) the weight of the resulting solution and (ii) the number of equivalents of acid or alkali in the solution.* *[I.I.T. 1976]*

Ans : $CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$ $H_2O \rightleftharpoons H^+ + OH^-$

At cathode : $Cu^{++} + 2e \rightleftharpoons Cu\downarrow$ *At anode :* $OH^- - e \rightleftharpoons OH$

$4OH = 2H_2O + O_2\uparrow$

Since H^+ and SO_4^{--} ions remain in solution, the solution becomes acidic.

(i) 1 Faraday of electricity liberates 1 gram-equivalent of Cu

∴ 0·01 Faraday of electricity liberates 0·01 gram-equivalent of Cu

0·01 gram-equivalent Cu = 0·01 × 31·75 = 0·3175 g Cu

Again, 1 Faraday liberates 1 gram-equivalent of O_2 = 8 g of O_2

0·01 Faraday liberates 0·01 gram-equivalent of O_2 = 8 × 0·01 = 0·08 g of O_2.

∴ Total weight of Cu and O_2 liberated during electrolysis = (0·3175 + 0·08) = 0·3975 g

Hence, the weight of the resulting solution after electrolysis = (10 − 0·3975) = 9·6025 g

(ii) 1 Faraday of electricity produces 1 gram-equivalent of H_2SO_4

∴ 0·01 Faraday of electricity produces 0·01 gram-equivalent of H_2SO_4

∴ 0·01 gram-equivalent of H_2SO_4 will remain in solution.

10 *A zinc rod weighing 25 g is immersed in 100 ml of 1 (M) $CuSO_4$ solution. After some time the molarity of the Cu^{++} ion in solution becomes 0·8. Calculate the molarity of SO_4^{--} ion in solution and the weight of Zn rod after the reaction. Calculate the molarity of Zn^{++} ion if a copper rod weighing 25 g be immersed in 50 ml of 2(M) $ZnSO_4$ solution for carrying out the above reaction for the same length of time.* *[I.I.T. 1976]*

Ans : $CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$ $Zn - 2e \rightleftharpoons Zn^{++}$ $Cu^{++} + 2e \rightleftharpoons Cu$

Weight of Cu in 100 ml of 1(M) $CuSO_4 = \frac{63{\cdot}5 \times 100}{1000} = 6{\cdot}35$ g

Weight of Cu in 100 ml of 0·8 (M) $CuSO_4$ = 0·8 × 6·35 = 5·08 g

Weight of Cu deposited = (6·35 − 5·08) = 1·27 g

We know 63·5 g of Cu is displaced by 65·4 g of Zn

1·27 g of Cu is displaced by $\frac{65{\cdot}4 \times 1{\cdot}27}{63{\cdot}5} = 1{\cdot}308$ g of Zn.

Hence, during reaction Zn rod loses a weight of 1·308 g

Hence the weight of Zn will be (25 − 1·308) = 23·692 g

According to equation SO_4^{--} ion does not change in concentration. Hence the concentration of SO_4^{--} ion will remain 1(M).

In the second case Zn is more electropositive than Cu i.e., Zn can give up electrons more readily than Cu. So Cu will neither give up electron nor Zn atom accept electron. So in this case there will be no reaction at all. The molarity of $ZnSO_4$ will remain the same i.e., 2(M).

11. *The total volume of H_2 and O_2 at the electrodes during the electrolysis of acidulated water is 16·8 ml at N.T.P. Calculate the quantity of electricity used.* *[I.I.T. 1971]*

Ans :

Volume of H_2 in 16·8 ml mixture = $\frac{2 \times 16{\cdot}8}{3} = 11{\cdot}2$ ml

Volume of O_2 in the mixture = 16·8 − 11·2 = 5·6 ml

We know, 11200 ml H_2 at N.T.P. are liberated by 96500 coulomb of electricity

11·2 " " " " " $\frac{96500 \times 11{\cdot}2}{11200} = 96{\cdot}5$ coulomb.

12. *Cadmium amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. For how long should electrolysis be carried out in order to prepare a 12% by weight of cadmium amalgam using 22·0 g of mercury and a current of 5 ampere ? (Cd = 112·0)* *[I.I.T. 1970]*

Ans : 12% cadmium amalgam means—

100 g of amalgam contain 88 g of Hg and 12 g of Cd

or, 88 g of Hg are mixed with 12 g of Cd

$\therefore$ 22 g of Hg are mixed with $\frac{12 \times 22}{88} = 3$ g of Cd

We know, $W = \frac{E.c.t}{96500}$; $E =$ Eq. wt. of Cd $= \frac{112}{2} = 56$

$$3 = \frac{56 \times 5 \times t}{96500} \quad \text{or, } t = \frac{3 \times 96500}{56 \times 5} = 1033{\cdot}92 \text{ second.}$$

13. *Calculate the weight of silver deposited at the cathode when 2·5 ampere current is passed through $AgNO_3$ solution for 1 hour. Also find the weight of copper and volume of hydrogen at N.T.P. when same amount of electricity is passed through $CuSO_4$ and H_2SO_4 solution joined in series with $AgNO_3$ solution.*

[Eq. wt. of Ag = 107·88 Cu = 31·75]

Ans : Applying the formula,

$$W = \frac{E.c.t}{96500} \qquad W = \text{weight of Ag.}$$

$$W = \frac{107{\cdot}88 \times 2{\cdot}5 \times 60 \times 60}{96500} = 10{\cdot}06 \text{ g}$$

Weight of Ag = 10·06 g

$$\frac{\text{Weight of Cu}}{\text{Weight of Ag}} = \frac{\text{Eq. wt. of Cu}}{\text{Eq. wt. of Ag}} \qquad \text{Weight of Cu} = \frac{10{\cdot}06 \times 31{\cdot}75}{107{\cdot}88} = 2{\cdot}9607 \text{ g}$$

$$\text{Again weight of hydrogen} = \frac{\text{Weight of Ag} \times \text{Eq. wt. of hydrogen}}{\text{Eq. wt. of Ag}}$$

$$= \frac{10{\cdot}06 \times 1{\cdot}008}{107{\cdot}88} = 0{\cdot}09399 \text{ g}$$

Volume of 0·09399 g of H_2 at N.T.P.

$$= \frac{22400 \times 0{\cdot}09399}{2{\cdot}016} = 1044{\cdot}33 \text{ ml}$$

14. *1·5 ampere of current is passed through 4 litres of 1·2 (M) $CuSO_4$ solution for 2 hours. Calculate the weight of substances liberated at the two electrodes. Calculate the concentration of the acid in the solution. [Eq. wt. of Cu 31·8]* *[W.B.H.S. '73, 83]*

Ans : Since Pt-electrode is used Cu is deposited at the cathode and O_2 is evolved at the anode.

96500 coulomb of electricity deposit 1 gram-equivalent of Cu = 31·8 g of Cu

$$1{\cdot}5 \times 2 \times 60 \times 60 \quad ,, \quad ,, \quad ,, \quad ,, \quad = \frac{31{\cdot}8 \times 1{\cdot}5 \times 2 \times 60 \times 60}{96500}$$

$$= 3{\cdot}5589 \text{ g of Cu}$$

Let W g be the weight of O_2 liberated at the anode

$$\therefore \frac{W}{3{\cdot}5589} = \frac{8}{31{\cdot}8} \qquad \text{or, } W = \frac{8 \times 3{\cdot}5589}{31{\cdot}8} \qquad \text{or, } W = 0{\cdot}8953 \text{ g}$$

96500 coulomb of electricity produce 1 gram-equivalent of H_2SO_4

$$1{\cdot}5 \times 2 \times 60 \times 60 \quad ,, \quad ,, \quad \frac{1{\cdot}5 \times 2 \times 60 \times 60}{96500}$$

$$= 0{\cdot}112 \text{ gram-equivalent of } H_2SO_4$$

Now 4 litre of the acid contains 0·112 gram-equivalent of H_2SO_4

1 " " " " " $\dfrac{0{\cdot}112}{4} = 0{\cdot}028$ gram-equivalent of H_2SO_4

$\therefore$ Normality of $H_2SO_4 = 0{\cdot}028$ (N)

15. *A certain quantity of current was passed through $CuSO_4$ solution for 1 hour when cathode showed an increase of 0·03 g. The milliammeter recorded 25 milliampere. Was the milliammeter defective ?*

Ans :

31·75 g of Cu is deposited by 96500 coulomb of electricity

$0{\cdot}03$ " " " " $\dfrac{96500 \times 0{\cdot}03}{31{\cdot}75}$ coulomb of electricity

We know, $Q = c.t$

$$\text{or, } c = \frac{Q}{t} = \frac{96500 \times 0{\cdot}03}{31{\cdot}75 \times 60 \times 60} = 0{\cdot}0253 \text{ amp} = 25{\cdot}3 \text{ milliampere.}$$

The milliammeter was defective. The correct reading will be 25·3 milliampere.

16. *On passing 0·5 ampere of current through $CuSO_4$ solution for 16 minutes and 5 seconds, 0·1589 g of Cu is deposited at the cathode. Calculate the value of F and charge of Cu^{++} ion. [At. wt. of Cu = 63·54]*

Ans : Quantity of electricity $= 0{\cdot}5 \times (16 \times 60 + 5) = 482{\cdot}5$ coulomb.

0·1589 g of copper is deposited by 482·5 coulomb

$31{\cdot}77$ " " " " " $\dfrac{482{\cdot}5 \times 31{\cdot}77}{0{\cdot}1589} = 96469{\cdot}6$ coulomb.

$\therefore$ 1 Faraday = 96469 coulomb.

Now 63·54 g (1 mole) of Cu contains $6{\cdot}023 \times 10^{23}$ Cu^{++} ions.

$31{\cdot}77$ " " " " $\dfrac{6{\cdot}023 \times 10^{23} \times 31{\cdot}77}{63{\cdot}54}$

$= 3{\cdot}01 \times 10^{23}$ Cu^{++} ions.

$3{\cdot}01 \times 10^{23}$ Cu^{++} ions contain 96469 coulomb of electricity

1 " " " contains $\dfrac{96469}{3{\cdot}01 \times 10^{23}} = 3{\cdot}204 \times 10^{-19}$ coulomb

$\therefore$ Charge of 1 Cu^{++} ion $= 3{\cdot}204 \times 10^{-19}$ coulomb.

17. *Silver is electro-deposited on a metallic vessel of surface area 800 cm^2 by passing a current of 0·20 ampere for 3 hours. Calculate the thickness of silver deposited. Given its density is 10·47 g/cc. (Ag = 107·92)* *[I.I.T. 1978]*

Ans :

Quantity of electricity $= 0{\cdot}20 \times 3 \times 60 \times 60 = 2160$ coulomb.

We know, $Ag^+ + e \rightarrow Ag$

Eq. wt. of Ag $= \dfrac{107{\cdot}92}{1} = 107{\cdot}92$

96500 coulomb of electricity deposit 107·92 g of silver

2160 " " " " $\dfrac{107{\cdot}92 \times 2160}{96500} = 2{\cdot}4156$ g of Ag

We know, Mass = Volume × density

Volume = Area × thickness

$\therefore$ Mass = Area × thickness × density.

$2{\cdot}4156 = 800 \times \text{thickness} \times 10{\cdot}47$

$$\text{Thickness} = \frac{2{\cdot}4156}{800 \times 10{\cdot}47} = 2{\cdot}88 \times 10^{-4} \text{ cm.}$$

Hence the thickness of Ag deposited $= 2{\cdot}88 \times 10^{-4}$ cm.

18. *The same quantity of electricity that liberates 4·316 g of Ag from $AgNO_3$ solution is passed into gold chloride solution. Calculate the weight of gold at the* *cathode and also the quantity of electricity passing. Given valency of gold in the salt = 3, Eq. wt. of Ag = 107·9 and Atomic weight of Au = 197·0* *[W.B.J.E. 1979]*

Ans : We know from Faraday's Law :—

$$\frac{\text{Weight of Ag}}{\text{Weight of Au}} = \frac{\text{Eq. wt. of Ag}}{\text{Eq. wt. of Au}}$$

$$\therefore \text{ Eq. wt. of Au} = \frac{197}{3} = 65{\cdot}66$$

$$\text{or, } \frac{4{\cdot}316}{\text{Weight of Au}} = \frac{107{\cdot}9}{65{\cdot}66}$$

$$\text{or, Weight of Au} = 2{\cdot}6264 \text{ g}$$

107·9 g of Ag are deposited by 96500 coulomb

$$4{\cdot}316 \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \quad \frac{96500 \times 4{\cdot}316}{107{\cdot}9} = 3860$$

Quantity of electricity passed = 3860 coulomb.

19. *A current of 3·7 ampere is passed for 6 hours between Nickel electrodes in 0·5 litre of a 2(M) solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of the electrolysis ? (At wt. of Ni = 58·7)* *[I.I.T. 1978]*

Ans : Weight of Ni = *W* g

$$\text{E.C.E of Ni} = \frac{58{\cdot}7}{2 \times 96500}$$

$$W = Z.c.t. = \frac{58{\cdot}7 \times 3{\cdot}7 \times 6 \times 60 \times 60}{2 \times 96500} = 24{\cdot}31 \text{ g}$$

0·5 lt of 2(M) $Ni(NO_3)_2$ contain 0·5 × 2 × 58·7 = 58·7 g of nickel

After electrolysis the solution will contain (58·7 – 24·31) g of nickel = 34·39 g of nickel.

$$\text{Strength of the solution} = \frac{34{\cdot}39}{58{\cdot}7} \times 2 = 1{\cdot}1717 \text{ (M)}$$

20. *A current of 80 microampere is passed through a solution of $AgNO_3$ for 32 minutes using Pt electrodes. A uniform single atom thick layer of silver is deposited covering 90% of the cathode surface. What is the total surface area of cathode, if each silver atom covers an area of $5{\cdot}4 \times 10^{-16}$ cm² ?* *[Tripura Jt. E. 1988]*

Ans :

Quantity of electricity = $80 \times 10^{-6} \times 32 \times 60 = 0{\cdot}1536$ coulomb

1 gram-equivalent of Ag = 1 gram-at. wt. of Ag = $6{\cdot}023 \times 10^{23}$ atoms of silver

$$[Ag^+ + e \rightarrow Ag]$$

96500 coulomb liberate $6{\cdot}023 \times 10^{23}$ atoms of Ag

$$0{\cdot}1536 \quad ,, \quad ,, \quad \frac{6{\cdot}023 \times 10^{23} \times 0{\cdot}1536}{96500} = 9{\cdot}58 \times 10^{17} \text{ atoms of Ag}$$

Covered area by Ag atom = $5{\cdot}4 \times 10^{-16} \times 9{\cdot}58 \times 10^{17} = 517{\cdot}32$ cm²

Now 90% area = 517·32 cm²

$$\therefore 100\% = \frac{517{\cdot}32 \times 100}{90} = 574{\cdot}8 \text{ cm}^2$$

Total surface area of the cathode = 574·8 cm²

21. *5 ampere current is passed through 100 ml of 0·8(M) $CuSO_4$ solution for 30 minutes. Calculate the weight of $CuSO_4$ remained in solution after electrolysis.* *[I.I.T. 1975]*

Ans : 1000 ml of 1 (M) $CuSO_4$ contain 159·5 g of $CuSO_4$

$$100 \;,,\; ,, \;\; 0{\cdot}8(M) \;\; ,, \qquad ,, \quad \frac{159{\cdot}5 \times 0{\cdot}8 \times 100}{1000} = 12{\cdot}76 \text{ g of } CuSO_4$$

Quantity of electricity passed = $5 \times 30 \times 60 = 9000$ coulomb

96500 coulomb deposite $^1/_2$ mole of copper

$$9000 \quad " \quad " \quad \frac{9000}{2 \times 96500} = 0{\cdot}04663 \text{ mole of copper.}$$

1 mole copper ≡ 1 mole of $CuSO_4$

$$0{\cdot}04633 \quad " \quad \equiv 0{\cdot}04663 \quad " \quad "$$

$$\equiv 0{\cdot}04663 \times 159{\cdot}5 = 7{\cdot}437 \text{ g of copper sulphate.}$$

Weight of copper sulphate remained in solution after electrolysis = $12{\cdot}76 - 7{\cdot}437$
$= 5{\cdot}323$ g

22. *0·4825 ampere current is passed through a metallic wire. Calculate the total number of electrons flown through a point of the wire in one second.* *[W.B.H.S. 1979]*

Ans : Quantity of electricity in 1 second = $0{\cdot}4825 \times 1 = 0{\cdot}4825$ coulomb.

$$\text{Charge of an electron} = \frac{F}{N} = \frac{96500}{6{\cdot}023 \times 10^{23}} = 1{\cdot}6 \times 10^{-19} \text{ coulomb.}$$

$1{\cdot}6 \times 10^{-19}$ coulomb of electricity is carried by 1 electron

$$0{\cdot}4825 \quad " \quad " \quad " \quad " \quad " \quad \frac{0{\cdot}4825}{1{\cdot}6 \times 10^{-19}} = 3{\cdot}016 \times 10^{18} \text{ electron.}$$

23. *1 gram-equivalent of H^+ ion carries that quantity of electricity which liberates 1 gram-equivalent of hydrogen gas. From this statement calculate the charge carried by 1 H^+ ion.* *[W.B.H.S. 1984]*

Ans : 1F or 96500 coulomb of electricity is required to discharge 1 gram-equivalent of hydrogen.

$$\text{Charge of 1 } H^+ \text{ ion} = \frac{F}{N} = \frac{96500}{6{\cdot}023 \times 10^{23}} = 1{\cdot}602 \times 10^{-19} \text{ coulomb.}$$

24. *The same quantity of electricity is passed through acidulated water and through a solution of the chloride of a metal X. As a result, 7·4 litre of H_2 at N.T.P. is liberated in the first case and 21 g of the metal X is deposited in the second case. Calculate the equivalent weight of X.* *[W.B.H.S. 1985]*

Ans : Weight of 7·4 litre of H_2 at N.T.P. = $0{\cdot}09 \times 7{\cdot}4 = 0{\cdot}666$ g

$$\frac{\text{Weight of the metal } X}{\text{Weight of hydrogen}} = \frac{\text{Eq. wt. of the metal}}{\text{Eq. wt. of hydrogen}}$$

$$\text{or, } \frac{21}{0{\cdot}666} = \frac{\text{Eq. wt. of the metal}}{1{\cdot}008}$$

$$\text{or, Eq. wt. of the metal } (X) = \frac{21 \times 1{\cdot}008}{0{\cdot}666} = 31{\cdot}78$$

25. *When 0·5 ampere of electricity is passed through a dilute solution of silver nitrate for 5 minutes, 0·2015 g of silver is deposited. Find out the electrochemical equivalent of silver.* *[W.B.H.S. 1991]*

Ans : Applying Faraday's first law of electrolysis.

$$W = Z.c.t$$

$$\text{or, } Z = \frac{W}{ct} = \frac{0{\cdot}2015}{0{\cdot}5 \times 5 \times 60} = \frac{0{\cdot}2015}{150} \; 0{\cdot}001343 \text{ g/coulomb.}$$

∴ E.C.E. of Ag = 0·001343 g/coulomb

26. *The density and E.C.E. of silver are 10·5 g cm^{-3} and $1{\cdot}118 \times 10^{-3}$ g/coulomb. If the charge of an electron is $4{\cdot}8 \times 10^{-10}$ e.s.u., calculate how many Ag atoms are present per ml.*

Ans : The charge on 1 Ag^+ ion = $4{\cdot}8 \times 10^{-10}$ e.s.u.
$= 1{\cdot}6 \times 10^{-19}$ coulomb.

$$Ag^+ + e \rightarrow Ag$$

When $1{\cdot}6 \times 10^{-19}$ coulomb of electricity is passed through Ag^+ ion only one atom of Ag will be discharged.

E.C.E. of Ag = $1{\cdot}118 \times 10^{-3}$ g/coulomb

Hence 1 coulomb of electricity will deposit $1{\cdot}118 \times 10^{-3}$ g

$1{\cdot}6 \times 10^{-19}$ " " " " $1{\cdot}6 \times 10^{-19} \times 1{\cdot}118 \times 10^{-3}$ g

$= 1{\cdot}6 \times 1{\cdot}118 \times 10^{-22}$ g

$\therefore$ Weight of 1 Ag atom $= 1{\cdot}6 \times 1{\cdot}118 \times 10^{-22}$ g

$$\therefore \text{Number of Ag atom/ml} = \frac{10{\cdot}5}{1{\cdot}6 \times 1{\cdot}118 \times 10^{-22}\text{ g}} = 5{\cdot}87 \times 10^{22}$$

27. *An aqueous solution of NaCl containing 5·85 g/litre of NaCl was electrolysed using Pt electrodes.* H_2 *and* Cl_2 *were set free at cathode and anode respectively. Find the pH of the solution after electrolysis.* *[Pune board 1981]*

Ans : The following reaction takes place when NaCl is subjected to electrolysis

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2\uparrow + Cl_2\uparrow$$

2 moles of NaCl give rise to 2 moles of NaOH

1 gram-eqivalent of NaCl ≡ 1 gram-equivalent of NaOH

$$\text{Gram-equivalent of NaCl} = \frac{5{\cdot}85}{58{\cdot}5} = 0{\cdot}1 \text{ gram-equivalent/litre}$$

$\therefore$ Gram-equivalent of NaOH = 0·1 gram-equivalent/litre

$\therefore [OH^-] = 0{\cdot}1$ (N)

$pOH = -\text{Log}[OH^-] = -\text{Log } 0{\cdot}1 = 1$

Since pH + pOH = 14

$\therefore$ pH = 14 − 1 = 13

Since after electrolysis the pH of the solution is 13, it will be highly alkaline.

28. *A current is passed for 5 hours through two cells arranged in series. The first cell contains an aqueous solution of gold and the second* $CuSO_4$ *solution. 9·85 g of gold is deposited in the first cell. If the oxidation number of the gold is + 3 calculate how much copper will be deposited in the second cell. Find also the quantity of electricity passed through the circuit [Au = 197, Cu = 63·5]* *[I.I.T. 1983]*

Ans : From Faraday's second law of electrolysis :—

$$\frac{\text{Weight of Au}}{\text{Weight of Cu}} = \frac{\text{Eq. wt. of Au}}{\text{Eq. wt. of Cu}}$$

$$\text{Eq. wt. of Au} = \frac{197}{3} = 65{\cdot}66$$

$$\text{Eq. wt. of Cu} = \frac{63{\cdot}5}{2} = 31{\cdot}75$$

$$\frac{9{\cdot}85}{\text{Weight of Cu}} = \frac{65{\cdot}66}{31{\cdot}75}$$

$$\text{Hence weight of Cu} = \frac{9{\cdot}85 \times 31{\cdot}75}{65{\cdot}66} = 4{\cdot}7629 \text{ g}$$

$$W = \frac{E.c.t}{96500} \qquad W = \text{Weight of Gold,}$$

$$\text{or, } 9{\cdot}85 = \frac{65{\cdot}66 \times c \times 5 \times 60 \times 60}{96500}$$

$$c = \frac{9{\cdot}85 \times 96500}{65{\cdot}66 \times 5 \times 60 \times 60} = 0{\cdot}804 \text{ ampere}$$

$\therefore$ Quantity of electricity $Q = c \times t = 0{\cdot}804 \times 5 \times 60 \times 60 = 14472$ coulomb.

29. *40 ml of 0·125 (M)* $NiSO_4$ *solution is electrolysed by a current of 0·05 ampere for 40 minutes.*

(i) Write equation for the reaction occuring at each electrodes.

(ii) How many coulombs of electricity passed through the solution ?
(iii) How many grams of the product deposited on the cathode ?
(iv) How long will the same current have to pass through the solution to remove completely the metal ions from the solution ?
(v) At the end of the electrolysis in (iv) how many grams of the product would appear at the anode ? [At. wt. of Ni = 59] *[I.I.T. 1978]*

Ans : (i) $NiSO_4 \rightleftharpoons Ni^{++} + SO_4^{--}$
$H_2O \rightleftharpoons H^+ + OH^-$
At Cathode : $Ni^{++} + 2e \rightarrow Ni \downarrow$
At Anode : $2SO_4^{--} - 4e \rightarrow 2SO_4$
$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2 \uparrow$

(ii) The quantity of electricity passed in the solution $= 0{\cdot}05 \times 40 \times 60 = 120$ coulomb.

(iii) Ni is deposited at the cathode.

Eq. wt. of Ni $= \frac{59}{2} = 29{\cdot}5$
96500 coulomb of electricity deposit 29·5 g of Ni
120 ” ” ” ” ” $\frac{29{\cdot}5 \times 120}{96500} = 0{\cdot}0367$ g of Ni

(iv) 1000 ml of 1 (M) $NiSO_4$ solution contain 59 g of Ni
1000 ml of 0·125 (M) ” ” ” $59 \times 0{\cdot}125$
40 ” ” ” ” ” ” $\frac{59 \times 0{\cdot}125 \times 40}{1000} = 0{\cdot}295$ g Nickel.
Again 29·5 g of Ni is deposited by 96500 coulomb
0·295 ” ” ” ” $\frac{96500 \times 0{\cdot}295}{29{\cdot}5} = 965$ coulomb.
Again Q = time in second × current in ampere
$\therefore$ time in second $= \frac{965}{0{\cdot}05} = 19300$ second = 5 hr 21 min 40 sec.

(v) At anode oxygen gas is evolved and H_2SO_4 is formed.
96500 coulomb of electricity liberate 8 g of oxygen
965 ” ” ” ” ” $\frac{8 \times 965}{96500} = 0{\cdot}08$ g of O_2
Again 96500 coulomb of electricity from 49 g of H_2SO_4
965 ” ” ” ” ” $\frac{49 \times 965}{96500} = 0{\cdot}49$ g of H_2SO_4

30. *How long a current of 3 ampere has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with a 0·005 mm thick layer ? Density of silver = 10·5 g/cm^3.* *[I.I.T. 1985]*

Ans : Volume of silver deposited = Area × thickness
$= 80 \times 0{\cdot}0005 = 0{\cdot}04$ cc.
Mass of Ag = Volume × density $= 0{\cdot}04 \times 10{\cdot}5 = 0{\cdot}42$ g
Quantity of electricity required to deposit 108 g of Ag = 96500 coulomb.
” ” ” ” ” 0·42 ” ” ” $\frac{96500 \times 0{\cdot}42}{108} = 375{\cdot}28$ coulomb.

Since $Q = c \times t$

$t = \frac{Q}{c} = \frac{375{\cdot}28 \text{ coulomb}}{3 \text{ amp}} = 125$ second = 2 min. 4 sec.
= 2 min 4 sec.

31. *During the discharge of a lead storage battery, the density of H_2SO_4 fell from 1·294 to 1·139 g/ml. Sulphuric acid of density 1·294 g/ml is 39% H_2SO_4 by weight and* *that of density 1·139 g/ml is 20% H_2SO_4 by weight. The battery holds 3·5 litre of the acid and the volume remained practically constant during the discharge.*

Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are :—

$$Pb + SO_4^{--} = PbSO_4 + 2e \text{ (charging)}$$
$$PbO_2 + 4H^+ + SO_4^{--} + 2e = PbSO_4 + 2H_2O \text{ (discharging)}$$
[I.I.T. 1986]

Ans : Density of 39% H_2SO_4 before discharging = 1·294 g/ml
„ „ 20% „ after „ = 1·139 g/ml

Number of moles of H_2SO_4 in the solution before discharging

$$=3500 \times 1{\cdot}294 \times \frac{39}{100} \times \frac{1}{98} = 18{\cdot}03 \text{ moles}$$

Number of moles of H_2SO_4 in the solution after discharging

$$=3500 \times 1{\cdot}139 \times \frac{20}{100} \times \frac{1}{98} = 8{\cdot}13 \text{ moles}$$

Number of moles of H_2SO_4 consumed by lead storage battery

$$=18{\cdot}03 - 8{\cdot}13 = 9{\cdot}90 \text{ moles.}$$

We know 1 mole of H_2SO_4 ≡ 98 g of H_2SO_4
≡ 2 gram-equivalent of H_2SO_4
∴ 9·90 moles of H_2SO_4 ≡ 2 × 9·90 gram-equivalent of H_2SO_4
1 gram-equivalent ≡ 1 Faraday ≡ 96500 coulomb
2 × 9·90 „ ≡ 2 × 9·90 Faraday = 2 × 9·90 × 96500 coulomb.

$$\text{Number of ampere hours for which the battery used} = \frac{2 \times 9{\cdot}90 \times 96500 \text{ coulomb}}{1 \text{ hour}}$$
$$= \frac{2 \times 9{\cdot}90 \times 96500}{3600} = 530{\cdot}75$$

32. *A 100 watt, 110 volt incandescent lamp is connected in series with an electrolyte cell containing $CdSO_4$ solution. What weight of cadmium will be deposited by the current flowing for 10 hours ?* *[I.I.T. 1987]*

Ans : We know, Volt × Current = Watt

$$\text{Current} = \frac{\text{Watt}}{\text{Volt}} = \frac{100}{110} = \frac{10}{11} \text{ amp.}$$

Total quantity of electricity passed through $CdSO_4$ solution

$$= \frac{10}{11} \times 10 \times 60 \times 60 \text{ coulomb.}$$

$$\text{Now } W = \frac{E.Q}{96500} \qquad E = \text{Eq. wt. of Cd} = \frac{112{\cdot}4}{2}$$

$$\text{Weight of Cd} = \frac{10 \times 10 \times 60 \times 60 \times 112{\cdot}4}{11 \times 96500 \times 2} = 19{\cdot}06 \text{ g}$$

33. *Determine the amount of electricity in coulomb required to deposit copper of thickness 10^{-3} cm on a plate having area of 100 sq cm using copper sulphate solution. [Density of Cu = 8·94 g/cc., Cu = 63·5]* *[W.B.J.E.E. 1991]*

Ans : We know, Mass = Volume × Density
Again Volume = Area × thickness
∴ Mass = Area × thickness × density
$= 100 \times 10^{-3} \times 8{\cdot}94 = 0{\cdot}894$ g

$$\text{Again from first law, } W = \frac{E.Q.}{96500} \quad E = \frac{63{\cdot}5}{2} = 31{\cdot}75$$

$$\therefore 0{\cdot}894 = \frac{31{\cdot}75 \times Q}{96500}$$

$$\text{or, } Q = \frac{0{\cdot}894 \times 96500}{31{\cdot}75} = 2717{\cdot}19 \text{ coulomb.}$$

34. *A current of 3 ampere was passed for 10,000 seconds through a solution of $CuSO_4$ when 9·8 g of copper was deposited at the cathode. Calculate the current efficiency.*

Ans : Quantity of electricity = 3 × 10,000 = 30,000 coulomb.

$$30000 \text{ coulomb of electricity deposit} = \frac{31{\cdot}75 \times 30{,}000}{96500} = 9{\cdot}87 \text{ g of copper}$$

$$\text{Current efficiency} = \frac{\text{Actual weight deposited}}{\text{Theoretical weight}} \times 100 = \frac{9{\cdot}8}{9{\cdot}87} \times 100 = 99{\cdot}29\%$$

35. *A current of 1·70 ampere is passed through 300 ml of 0·160 (M) solution of $ZnSO_4$ for 230 seconds with a current efficiency of 90 percent. Find out the molarity of Zn^{++} ion after the deposition of Zn. Assume the volume of the solution to remain constant during the electrolysis. [At. wt. of Zn = 65·4]* *[I.I.T. 1991]*

Ans : Number of gram-equivalent of Zn^{++} ions present before electrolysis

$$= \frac{300 \times 0{\cdot}16 \times 65{\cdot}4}{1000 \times 32{\cdot}7} = 0{\cdot}096 \text{ gram equivalent}$$

Quantity of electricity passed through the $ZnSO_4$ solution with current efficiency of

$$90\% = 1{\cdot}70 \times 230 \times \frac{90}{100} = 351{\cdot}9 \text{ coulomb.}$$

$$\text{Number of gram-equivalent of Zn deposited after electrolysis} = \frac{351{\cdot}9}{96500}$$

$$= 0{\cdot}003647 \text{ gram-equivalent}$$

$[Zn^{++}]$ left in solution after electrolysis = (0·096 − 0·003647) gram-equivalent

= 0·09235 gram-equivalent

$$\text{Concentration of } Zn^{++} \text{ ion} = \frac{{\cdot}09235 \times 1000}{300} \text{ (N)} = \frac{0{\cdot}09235 \times 1000}{300 \times 2} \text{ (M)} \doteq 0{\cdot}154 \text{ (M)}$$

36. *19·0 g of molten $SnCl_2$ is electrolysed for sometime using inert electrodes until 0·119 g of Tin is deposited at the cathode. No substance is lost during electrolysis. Find the ratio of the weight of $SnCl_2$: $SnCl_4$ after electrolysis. [Sn = 119]* *[I.I.T. 1981]*

Ans : The reaction

$$\begin{array}{ccccc} 2\,SnCl_2 & \rightarrow & Sn & + & SnCl_4 \\ 380\text{ g} & & 119\text{ g} & & 261\text{ g} \end{array}$$

119 g of Sn is obtained from 380 g of $SnCl_2$

$$0{\cdot}119 \quad " \quad " \quad " \quad " \quad \frac{380 \times 0{\cdot}119}{119} = 0{\cdot}38 \text{ g of } SnCl_2$$

Before electrolysis 19·0 g of $SnCl_2$ was present.

Weight of $SnCl_2$ after electrolysis = 19 − 0·38 = 18·62 g

Similarly weight of $SnCl_4$ when 0·119 g of Sn is deposited during electrolysis

$$= \frac{261 \times 0{\cdot}119}{119} = 0{\cdot}261 \text{ g}$$

Ratio of $SnCl_2$: $SnCl_4$ = 18·62 : 0·261 = 71·34 : 1

37. *Assume that impure copper electrode contains only iron, silver and gold as impurities. When 140 ampere of current is passed for 482 seconds through a solution containing the above, the weight of anode is decreased by 22·26 g while cathode showed an increase of weight of 22·011 g. Find the percentage of iron present in the mixture.*

Ans : Copper is electrodeposited at the cathode

Hence the increase in weight of cathode = Weight of Cu deposited = 22·011 g

∴ Total weight of Fe, Au and Ag is due to the difference between decrease in the mass of anode and increase in the mass of cathode

= 22·26 − 22·011 = 0·249 g

Gold and silver remain as anode mud while both Cu and Fe are oxidised to bivalent State

$$M - 2e \rightleftharpoons M^{++} \text{ i.e., } Fe - 2e \rightleftharpoons Fe^{++}$$

2 electrons are required for the electrodeposition of the metal.

Now quantity of electricity passed = 482 × 140

$$= 67480 \text{ coulomb}$$

$$\text{No of gram-equivalent of } Fe^{++} = \frac{67480}{96500}$$

$$\text{,, ,, ,, moles of Fe} = \frac{67480}{2 \times 96500} = 0{\cdot}35$$

Weight of Fe = 0·35 × 56 = 0·20 g

$$\% \text{ of Fe} = \frac{0{\cdot}20 \times 100}{22{\cdot}011} = 0{\cdot}90\%$$

Hence % of Fe originally present = 0·90

38. *In carrying out the following reaction—*

$2MnO_2 + Zn^{++} + 2e \rightarrow Zn(MnO_2)_2$ the current obtained was $4{\cdot}0 \times 10^{-4}$ ampere. If 14·0 g of MnO_2 are used. Find the time of withdrawing current due the reaction [Mn = 54·9]

Ans·: $\underset{\text{2 moles}}{2MnO_2} + Zn^{++} + \underset{\text{2 Faradays}}{2e} \rightarrow Zn(MnO_2)_2$

or, 2 × [54·9 + 32] g of MnO_2 generate 2 × 96500 coulombof electricity

∴ 14 g of MnO_2 will generate

$$= \frac{2 \times 14 \times 96500}{2 \times 86{\cdot}9} = 15546{\cdot}6 \text{ coulomb.}$$

$$Q = c \times t \qquad \text{or, } t = \frac{Q}{c} = \frac{15546{\cdot}6}{4 \times 10^{-4}} = 3886{\cdot}5 \times 10^4 \text{ second}$$

Time for which current can be withdrawn = 38·865 × 10^6 second.

39. *A solution of 1(M) $CuSO_4$ is electrolysed between copper electrodes by a current of 10A for 965 second at 25°C. What changes occur at both the electrodes and in the solution ?* [W.B. J. E. '93]

Ans : The reaction at the respective electrodes are—

Cathode : $Cu^{++} + 2e \rightarrow Cu\downarrow$

Anode : $Cu \quad - 2e \rightarrow Cu^{++}$

Quantity of electricity = 10 × 965 = 9650 coulomb.

$$= \frac{9650}{96500} = 0{\cdot}1 \text{ Faraday}$$

$$\text{Gram-equivalent of Cu} = \frac{63.5}{2}$$

$$\text{Weight of copper deposited at cathode} = 0{\cdot}1 \times \frac{63{\cdot}5}{2} = 3{\cdot}175 \text{ g}$$

This amount of copper is deposited at the cathode and same quantity of copper dissolves from anode into the electrolyte. Hence the concentration of the solution remains unchanged.

40. *Molten aluminium chloride is electrolysed with a current of 0·5 ampere to produce 27g of aluminium.*

(i) How many gram equivalent of aluminium were produced ? (ii) How many gram atoms of aluminium were produced ? (iii) How many atoms of aluminium were produced ? (iv) How many electrons were produced ? (v) What is the number of faraday of electricity consumed ? (vi) How long did the electrolysis take place ? (vii) How many litres of Cl_2 at S.T.P. were produced ?

Ans : (i) The relevant reaction at the cathode is $Al^3 + 3e \rightarrow Al$

∴ gram-equivalent of Al = 27/3 = 9 g

9 g of Al = 1 gram-equivalent of Al
$\therefore$ 27 g of Al = 27/9 = 3 gram-equivalent of Al.
(ii) The atomic wt. of = 27
$\therefore$ 27 g of Al = 1 gram-atom of Al
(iii) 1 gram-atom of Al contains $6{\cdot}0^{23} \times 10^{23}$ atoms
$\therefore$ 27 g of Al (1 gram atom) contains $6{\cdot}023 \times 10^{23}$ atoms
(iv) In the formation of 1 Al atom 3 electrons are taken by Al^{3+} ion
$\therefore$ Total No. of electrons = $3 \times 6{\cdot}023 \times 10^{23} = 18{\cdot}069 \times 10^{23}$
(v) Since 1 gram-equivalent of Al is liberated by 1 faraday
$\therefore$ 3 gram-equivalent of Al is liberated by 3 faraday.
(vi) Let the time taken is *t* seconds total quantity of electricity = $0{\cdot}5 \times t$ coulomb.
but the electricity consumed is 3 faraday = 3×96540 coulomb

$$\therefore\ 0{\cdot}5t = 3 \times 96540\ ;\quad \text{or, } t = \frac{3\times96540}{0{\cdot}5}$$

or, $t = 570240$ seconds.

• Exercises •

1. Write explanatory notes indicating the differences between electrolytes and non electrolytes. Give two examples of each. *[W.B.H.S. '80]*

2. Write notes on—(a) Electrolytes (b) Electrolysis (c) Anode and cathode (d) Cation and anion.

3. Give on account of Arrhenius' theory of electrolytic dissociation. Comment on the statement : Arrhenius' 'theory is hardly tenable for strong electrolytes'. *[W.B.H.S. '84]*

4. Explain with examples what do you understand by strong electrolytes and weak electrolytes.

5. Compare thermal dissociation with electrolytic dissociation.

6. State what changes occur at the electrodes and in the solutions when electric current is passed through

(a) $CuSO_4$ solution with platinum electrodes (b) $CuSO_4$ solution with copper electrodes (c) silver nitrate solution with platinum electrodes (d) silver nitrate solution with silver electrodes (e) alumina dissolved in cryolite with graphite electrodes (f) aqueous solution of caustic soda with nickel electrodes (g) sodium chloride solution with graphite electrodes (h) 60% H_2SO_4 with platinum electrodes (i) fused NaCl with graphite electrodes (j) sodium chloride solution with mercury cathode and graphite anode.

What substances and in what quantities will be formed at the electrodes in each case when one Faraday of electricity is passed through each electrolyte ?

7. (a) State and explain Faraday's laws of electrolysis *[W.B.H.S. '94]*, (b) With the help these two laws how would you obtain (i) a definition of electro-chemical equivalent (ii) a relation between electro-chemical equivalent and chemical equivalent. *[W.B.H.S. '92]*

8. With the help of Faraday's two laws of electrolysis prove that the quantity of electronic charge on one ion of an element in aqueous solution is *n*F/N, where, n = valency of the element, N = the Avogadro's number and F = Faraday. What is the special significance of F/N ? *[Jt. Ent. '90]*

9. (a) With the help of Faraday's law, prove that the charge carried by an ion in an aqueous solution is the electronic charge multiplied by a small whole number.

(b) Show that $E = ZF$, where E = chemical equivalent, Z = electro-chemical equivalent of an element and F = faraday. *[W.B.H.S. '94]*

(c) How many grams of sodium and chlorine are deposited at the electrodes by passing one Faraday of electricity through fused NaCl ? *[W.B.H.S. '94]*

10. What do you mean by 'electro-chemical equivalent' and 'chemical equivalent' of an element ? *[Jt. Ent. '91]*

11. Deduce an expression by combining Faraday's two laws of electrolysis. *[Jt. Ent. '82, '84] [H.S. '84]* How can you apply the expression in determining the quantity of electricity ?

12. What is Faraday ? State its significance. Find out the value of one faraday in coulomb by applying Faraday's law. *[W.B.H.S. '82] [Jt. Ent. '89]*

13. Prove that one Faraday of electricity is required to liberate one gram equivalent of a substance at the electrode.

14. Deduce a relation between Faraday, Avagadro number and the charge of an ion. Find out the amount of charge carried by monovalent and divalent ions. What is the charge of Al^{3+} ion ?

15. (a) What is the total charge in coulomb carried by Avogadro number of electrons ? *[W.B.H.S. '94]*

(b) How many electrons are there in (i) one Faraday of electricity (ii) one mole of electron ?

(c) Explain the method to determine the Avogadro number (N) from Faraday's law of electrolysis.

16. Explain why —

(i) Same substances are liberated at the cathode and anode during the electrolysis of aqueous solution of caustic soda and dilute solution of sulphuric acid separately.

(ii) An aqueous solution of NaCl conducts electricity but that of cane sugar can not conduct electricity. *[W.B.H.S. (T) '83]*

(iii) Metallic sodium is not liberated at the cathode when an aqueous solution of sodium chloride is electrolysed.

(iv) The conductivity of 1 (M) HCl is greater than that of 1 (M) acetic acid solution.

(v) Pure water is a bad conductor of electricity but acidulated or alkaline water is a good conductor of electricity. *[Jt. Ent. '80]*

(vi) K^+ ion is more stable than K atom.

(vii) All electrolytes are conductor of electricity, but all conductors are not electrolytes. *[Jt. Ent. '89]*

(viii) On prolonged electrolysis of copper sulphate solution, hydrogen is liberated at the cathode instead of copper.

(ix) On the electrolysis of copper sulphate solution using copper electrodes, the copper anode loses its weight.

(x) Anhydrous HCl can not conduct electricity but an aqueous solution of HCl is a good conductor.

(xi) The properties of an ion differ from that of the atom from which the ion is derived.

(xii) The conductivity of H_2SO_4 and HCN is different.

(xiii) In the process of electrolysis, the current brings about oxidation-reduction.

(xiv) Dilute H_2SO_4 is more stronger than concentrated H_2SO_4.

(xv) Graphite anode is used in the electrolysis of fused NaCl.

(xvi) When the aqueous solution containing a mixture of $CuSO_4$ and $ZnSO_4$ is electrolysed with platinum electrodes, Cu is liberated at the cathode.

17. (a) Prove that the fundamental unit of charge = F/N where F = faraday, and N = Avogadro number.

(b) Deduce a relation between the mass of substance and its electro-chemical equivalent.

18. Explain the statement—'Anions and cations conduct electricity in the same direction'.

19. What is Faraday ? Write down the equation relating Faraday (F), Avogadro number (N) and charge of an electron (e). *[W.B.H.S. '92]*

20. Answer the following—

(a) Why thermal dissociation and electrolytic dissociation are not same ?

(b) Explain why Na reacts violently when comes in contact with water but Na^+ ion does not react with water ?

(c) Explain why the cations and anions are liberated in equivalent amount at the electrodes though their speed differ.

(d) What is meant by one mole of electricity ?

(e) In the electrolysis of an electrolyte why reduction occurs at the cathode and oxidation occurs at the anode ?

Objective type of questions :

21. Select the correct answer (answers)—

(i) The number of electrons involved in the reaction when one Faraday of electricity is passed through an electrolyte in aqueous solution is

(a) 12×10^{46} (b) 96540 (c) $1{\cdot}6 \times 10^{-19}$ (d) $6{\cdot}023 \times 10^{23}$ [***Ans.*** (d)]

(ii) According to Faraday's first law of electrolysis, mass (M) of an ion liberated is equal to

(a) ZE (b) ZC (c) Zct (d) Zct/nF [***Ans.*** (c)]

(iii) The electric charge for electrode diposition of one gram equivalent of a substance is

(a) 1 ampere sec^{-1} (b) 965000 coulomb sec^{-1} (c) 1 ampere $hour^{-1}$ (d) charge on one mole of electron. [***Ans.*** (d)] *[I.I.T. '84]*

(iv) When electric current is passed through acidulated water, 112 ml of H_2 at N.T.P. is liberated at the cathode in 965 seconds. The current passed in ampere is —

(a) 1·0 (b) 0·5 (c) 0·1 (d) 2·0 [***Ans.*** (a)] *[M.L.N.R. '91]*

(v) Faradays laws of electrolysis are related to the

(a) atomic number of the cation (b) atomic number of anion (c) equivalent weight of the electrolyte (d) speed of the cation. [***Ans.*** (c)] *[I.I.T. '89]*

(vi) The reaction at the cathode during electrolysis of dilute H_2SO_4 with platinum electrodes is —
(a) oxidation (b) reduction (c) both oxidation and reduction (d) neutralisation.
[***Ans.*** (b)] *[M.L.N.R. '88]*

(vii) When molten NaCl is electrolysed, the reaction occuring at the anode is —
(a) Na^+ ions are oxidised (b) Cl^- ions are oxidised (c) both Na^+ and Cl^- ions are oxidised (d) Cl^- ions are reduced. [***Ans.*** (b)]

(viii) When dilute H_2SO_4 is electrolysed between Pt electrodes, the gas liberated at the anode will be —
(a) SO_2 (b) SO_3 (c) H_2 (d) O_2 [***Ans.*** (d)]

(ix) A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$, $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of reduction potentials in volts are $E^0_{Ag/Ag^+} = +0{\cdot}8$, $E^0_{2Hg/Hg_2^{++}} = 0{\cdot}79$, $E^0_{Cu/Cu^{++}} = 0{\cdot}34$, $E^0_{Mg/Mg^{++}} = -2{\cdot}37$.
With the increasing voltage, the sequence of deposition of metals on cathode will be
(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag (c) Ag, Hg, Cu (d) Cu, Hg, Ag, Mg [***Ans.*** (c)] *[I.I.T. '84]*

(x) Copper sulphate solution is electrolysed using copper electrodes, the reaction taking place at the anode is
(a) $H^+ + e \rightarrow H$, (b) $SO_4^{2-}\,(aq) - 2e \rightarrow SO_4$, (c) $Cu^{2+}\,(aq) + e \rightarrow Cu\,(s)$, (d) $Cu\,(s) - 2e \rightarrow Cu^{2+}\,(aq)$
[***Ans.*** (d)]

22. Fill up the blanks :

(i) Electrolysis involves ________ at the anode and ________ at the cathode.

(ii) Electrolysis of molten sodium hydride liberates ________ at the ________. *[I.I.T. '89]*

(iii) The electrical conductivity of a solution of acetic acid will be ________ if a solution of NaOH is added. *[I.I.T. '87]*

(iv) ________ is the smallest unit of electricity.

(v) The weights of various ions liberated by passing the same current through different electrolytes are in the ratio of their ________. *[I.I.T. '75]*

(vi) During electrolysis, 48250 coulombs of electricity will deposit ________ gram-equivalents of silver from Ag^+ ions. *[I.I.T. '73]*

(vii) During the electrolysis of $CuSO_4$ solution with copper electrodes half gram atom of copper is oxidised to Cu^{2+} ion when ________ coulombs of electricity is passed. *[I.I.T. '73]*

(viii) The electrolysis of an aqueous solution of NaCl, ________ ions are discharged in preference to ________ ions at platinum cathode.

Numerical problems :

1. When 0·5 ampere of electricity is passed through a dilute solution of silver nitrate for 5 minutes, 0·2015 g of silver is deposited. Find out the electro-chemical equivalent of silver.
[***Ans.***0·00134] [*H.S. '91]*

2. What volume of 0·05 (N) H_2SO_4 is required to neutralise the alkali produced after passing 0·4 ampere of electricity in dilute NaCl solution for 5 minutes ?
[***Ans.***24·816 ml [*H.S. '92]*

3. 1·5 ampere current is passed through 100 ml of 0·4 (M) $CuSO_4$ solution for 50 minutes. The reactions at the electrodes are—

At cathode : $Cu^{2+} + 2e \rightarrow Cu\downarrow$; *At anode* : $2H_2O \rightarrow O_2 + 4H^+ + 4e$

Calculate the molar concentration of Cu^{2+}, H^+ and SO_4^{2-} ions assuming volume of the solution does not change. [***Ans.*** 0·167 (M)] *[Jt. Ent. '89]*

4. Chromium metal can be plated out from an acetic solution containing CrO_3 according to the following equation—

$$CrO_3\,(aq) + 6H^+\,(aq) + 6e^- \rightarrow Cr(s) + 3H_2O$$

Calculate, (i) how many grams of Cr will be plated out by 24,000 coulombs, (ii) how long will it take to plate out 1·5 g of Cr by using 12·5 amp current ? [***Ans.*** 2·155 g, 1336 sec.] *[I.I.T. '93]*

[Hints:

$$w = \frac{Ect}{96500} = \frac{52 \times 24000}{6 \times 96500}\ g$$

$$t = \frac{WF}{Ec} = \frac{1{\cdot}5 \times 96500 \times 6}{52 \times 12{\cdot}5}\ sec.]$$

5. An aqueous solution of NaCl on electrolysis gives H_2, Cl_2 and NaOH according to the reaction $2Cl^-\,(aq) + 2H_2O = 2OH^-\,(aq) + H_2\,(g) + Cl_2\,(g)$.
A direct current of 25 amperes with a current efficiency of 62% is passed through 20 litres of NaCl solution (20% by weight). Write down the reactions taking place at the anode and cathode. How long will it take to produce 1 kg of Cl_2 ? What will be the molarity of the solution with respect to OH^- ion (assume no loss due to evaporation). [***Ans.*** 97 hr 26 mint 2 sec., 2·89] *[I.I.T. '92]*

6. If 4 amperes current is passed for 20 minutes through 1(M) $CuSO_4$ solution, what will be the concentration of Cu^{++} ion in the final solution ? [***Ans.*** 61·92 g lit^{-1}]

7. 0·268 ampere current is passed through a solution of a metallic ion for 30 minutes. When 0·266 g of the metal is deposited. The specific heat of the metal 0·0565. Find the oxidation number of the metallic ion and the atomic weight of the metal. [*Ans.* +2, 106·4 g]

8. By passing 0·25 ampere current through $CuSO_4$ solution for 1 hour, 0·295 g of copper is deposited. Find the equivalent weight of copper. (F = 96500 coulomb) [*Ans.* 31·63]

9. The same current is passed through acidulated water and an aqueous solution of a metallic chloride for the same time, when 7·4 litres of H_2 at N.T.P. is liberated and 21 g of the metal is deposited. The specific heat of the metal is 0·094. Find the atomic weight of the metal and tne formula of its chloride. [*Ans.* 63·56 ; MCl_2]

10. How many copper atoms will be liberated at the electrode when 0·5 ampere current is passed for 26 minutes through $CuSO_4$ solution with platinum electrodes ? [*Ans.* $2·434 \times 10^{21}$]

11. (a) A solution of 1 (M) $CuSO_4$ solution is electrolysed between copper electrodes by a current of 10 ampere for 965 seconds at 25°C. What changes occur at both the electrodes and in the solution ?

(b) Describe the changes that would occur if the electrolysis is carried out as in (a) with 2(M) $CuSO_4$ solution at 50°C.

(c) Describe the changes that would occur (at the electrodes and in solution, if the electrolysis is carried out, as in (a) using both the electrodes as Pt-electrode [At. wt. of Cu = 63·5] [*Jt. Ent.* '93]

[*Ans.* (a) 3·175 g of Cu is deposited at the cathode and 3·175 g of Cu dissolves into solution from the anode. Thus cathode gains 3·175 g and anode loses 3·175 g. Concentration of the solution remains unchanged at 1(M).

(b) Chemical changes depend on the quantity of electricity and not on the concentration, so the changes will be same as in (a).

(c) Cathode gains 3·175 g due to deposition of Cu. No change in the anode but 0·8 g O_2 is liberated at the anode and 4·9 g of H_2SO_4 is produced in the solution 7·975 g of $CuSO_4$ is removed from the original $CuSO_4$ solution.]

12. Calculate the volume of the electrolytic gas at N.T.P. liberated, when 10 ampere current is passed through acidified water for 100 secs. [*Ans.* H_2=116 ml, O_2=58 ml] [*H.S.* '94]

13. (a) A current of 2 amperes was passed through N/10 solution of $CuSO_4$ for 16 minutes 5 secs. Calculate the amount of copper deposited on the cathode. (b) What will be the effect when the same current is passed (i) through are N/5 solution of copper sulphate for the same time and (ii) through N/10 solution of the same substance for 32 minutes and 10 seconds ?

[*Ans.* Cu deposited 0·636 g. (i) amount of Cu will remain same, (ii) 1·272 g]

14. The same electric current is passed in series through acidulated water and an aqueous solution of a metallic chloride for the same time. 112 ml of hydrogen at NTP and 0·325 g of the metal are liberated at the respective cathodes. The specific heat of the metal is 0·094. Find the atomic weight of the metal. [*Ans.* 65]

15. 1·0 ampere current is passed through 2 litre of 1·2 (M) $CuSO_4$ solution for 2 hours. Find the amount of substances liberated at electrodes. Find the normality of the produced acid in the final solution. [*Ans.* Cu 2·3689 g, O_2 0·5969 g, 0·037(N)]

16. 0·5 ampere current is passed through $CuSO_4$ solution for 30 minutes when 0·2964 g of copper is deposited at the cathode. Find the atomic weight of copper. [*Ans.* 63·56] [*I.I.T.* '72]

17. A metallic oxide contains 12·5% of oxygen. The oxide is converted to chloride and 0·965 ampere current is passed through the solution of the chloride for 5 hours. Find the weight of the liberated metal. What is the valency of the metal ? (At. wt. of the metal is 112) [*Ans.* 10·08 g ; 2]

18. 0·01 F electricity is passed through a concentrated solution of $CuSO_4$ containing 10 g of $CuSO_4$. (i) After the electrolysis what will be the weight of the solution ? (ii) Find the gram equivalent of the acid or alkali produced. In this electrolysis Cu is used as cathode and Pt is used as anode.

[*Ans.* (i) 9·6025 g ; (ii) 0·01 gm eq of acid] [*I.I.T.* '76]

19. How long will it take for a current of 4 amperes to liberate 10 g of Cu from a 1·2 molar solution of copper sulphate ? (Cu = 63) [*Ans.* 2 hrs 7 mints 38 sec]

20. The quantity of electricity which is required for the electrolysis of 454 g of water, can deposite 1480 g of a metal at the cathode. The atomic weight of the metal is 58·7. Find the valency of the metal and the formula of its sulphate. [*Ans.* Valency = 2, MSO_4]

21. When 1 ampere current is passed through a solution of a salt of a metal M for 965 seconds, 0·406 g of the metal is liberated at the cathode. The vapour density of the metallic chloride is 114. Find the atomic weight of the metal. [*Ans.* 121·8]

22. How many H^+ and Cu^{++} ions are transformed into the respective atoms by passing a current of 2 amperes for 1 minute ? ($N = 6·023 \times 10^{23}$) [*Ans.* $7·49 \times 10^{20}$; $3·74 \times 10^{20}$]

23. On passing electric current through a solution of a salt of metal M, the reaction at the cathode is $M^{2+} + 2e \rightarrow M$. The atomic weight of M is 65. Calculate the chemical equivalent and electro-chemical eq. of M. [*Ans.* E = 32·5, E.C.E = $3·36 \times 10^{-4}$]

24. Copper is electro deposited on a cathode having surface area of 1500 cm^2 by passing a current of 2 amperes for 5 hours. Calculate the thickness of the copper deposited (E.C.E. of Cu = 0·0003294 g/coulomb and density of Cu = 8·9 g/cm^3. [*Ans.* 8·88 × 10^{-4} cm]

25. How many electrons pass through the solution to the anode when 2·00 g of copper is deposited by passing current through $CuSO_4$ solution ? (Cu = 63·5 ; Faraday = 96500 coulombs). [*Ans.* 3·79 × 10^{22}]

26. What is charge in coulombs on the N^{3-} ion ? [*Ans.* 4·8 × 10^{-19} coulombs]

27. The density of copper is 8·94 g cm^3. Find out the number of coulombs needed to plate an area of 10 cm × 10 cm to a thickness of 10^{-2} cm using $CuSO_4$ solution as electrolyte.
[*Ans.* 27171·97 coulombs] [*I.I.T.* '79]

28. During the electrolysis of an aqueous solution of NaCl, 0·1 g of chlorine is liberated. Calculate the volume of hydrogen measured at 15°C and 745 mm pressure which will be liberated at the same time.
[*Ans.* 33·95 ml]

29. (a) A current deposits 5 g of Cu in 1930 minutes from a solution of Cu^{2+} ions. What the strength of the current is amperes ?

(b) How many grams of copper will the same current deposit during the same time from a solution of Cu^+ ions ? (At wt. of Cu = 63·5) [*Ans.* 0·131 amp., 10 g] [*I.I.T.* '77]

30. When 8040 coulombs of electricity is passed through a molten metal fluoride of formula MF_2, 3·652 g of metal is deposited. What is the atomic weight of the metal ? How many electrons have passed through the cell in the deposition of the metal ? [*Ans.* 49·66 ; 5·01 × 10^{22}]

31. Calculate the amount of water which is to be decomposed electrically to give enough H_2 at 30°C and 760 mm pressure to fill a baloon of capacity 1 million litres. [*Ans.* 724·09 kg]

32. An acidic solution of Cu^{2+} salt containing 0·4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for 7 minutes more with the volume the solution kept at 100 ml and the current at 1·2 ampere. Calculate the volume of the gases evolved of NTP during the entire electrolysis. [*Ans.* H_2 = 58·58 ml, O_2 = 99·79 ml] [*I.I.T.* '89]

33. An electric current is passed through (i) a solution of $AgNO_3$ and (ii) a solution of 10 g of $CuSO_4$, $5H_2O$ crystals in 500 ml of water. Platinum electrodes are used in each case. After 30 minutes it was found that 1·307 g of Ag was deposited. What was the concentration of copper expressed as grams of copper per litre in $CuSO_4$ solution after electrolysis ? (Cu = 63·5 ; Ag = 108) [*Ans.* 4·321 g/litre]

34. Find out the charge in coulombs on one gram ion of N^{3-} [*Ans.* 2·89 × 10^5 coulombs]

35. How many atoms of Ca will be deposited from molten $CaCl_2$ when a current of 25 milli ampere is passed through it for 60 seconds ? [*Ans.* 4·68 × 10^{18}]

36. How long will it take for a current of 1·25 amperes to deposit Cu of thick 0·1 mm on a circular copper plate of diameter 5 cm. Density of copper is 8·9 g/cc and E.C.E of Cu = 0·00033 g/coulomb.
[*Ans.* 1 hr 10 mints 38 secs]

37. Find the number of chlorine atoms liberated when a current of 300 milliamper is passed through hydrochloric acid for 60 seconds. [*Ans.* 1·12 × 10^{20}]

38. How many electrons are gained by 2 g of Cu^{2+} ions as a result of electrolysis ? [*Ans.* 3·78 × 10^{22}]

39. What volume of 0·1 (M) HCl would be required to neutralise the sodium hydroxide produced at the cathode which was obtained by passing a current of 2 amperes through an aqueous solution of sodium chloride for one hour ? [*Ans.* 746·2 ml]

40. Acidulated water is electrolysed in a cell and the volume of the electrolytic gas thus obtained is 16·8 ml at N.T.P. Calculate the quantity of electricity that was passed through the acidulated water ?
[*Ans.* 96·5 coulomb]

CHEMICAL EQUILIBRIUM AND LAW OF MASS ACTION

10

Introduction :

It is true that rearrangement of atoms in a molecule finally leads to a chemical reaction i.e., the products are more stable than the reactants but the pertinent question of a student is—why some chemical reactions take place while some do not ? In the reactions $A + B \rightarrow C + D$, the reactants A and B combine to form the products C and D but why not C and D have strong affinity to form A and B ? Again some reactions are rapid while some are extremely slow, some reactions are even explosive. Some reactions are catalysed by external agent while others do not have such influence. Again some reactions are complete and quantitative while some others are incomplete.

Whether a particular reaction is likely to occur or not, can be ascertained from the study of thermodynamics, change of heat content (ΔH) as well as free energy changes (ΔG) during the course of a chemical reaction. The exact theoretical consideration depends upon the detailed study of the **reaction mechanism** under the domain of chemical kinetics (vol II) where the rates of reaction (slow or fast) i.e., "How fast" a chemical reaction proceeds will be studied. In the present chapter our main objective is to answer "how far" a chemical reaction proceeds, whether a reaction is complete or incomplete and the influence of environment i.e., temperature, pressure, concentration etc., on a reversible reaction.

10.1. Concept of reversible reaction.

When an aqueous solution of sodium carbonate is added to an aqueous solution of calcium chloride immediately white $CaCO_3$ is precipitated out.

$$Na_2CO_3 + CaCl_2 = 2NaCl + CaCO_3\downarrow$$

Now the question is, whether sodium chloride will react with calcium carbonate to form sodium carbonate and calcium chloride.

According to old school of thoughts chemical reaction is the result of affinity of one atom for the others leading to the formation of a stable compound. Therefore the compound will not dissociate into original atom. In the above reaction Na has a strong affinity towards Cl atom ; similarly Ca atom has strong affinity towards CO_3 radical. Hence is the formation of NaCl and $CaCO_3$. Consequently this pair will not combine to reform sodium carbonate and calcium chloride. This is precisely what happens i.e., they never react under ordinary condition to form $CaCl_2$ and Na_2CO_3.

Large deposit of *TRONA* (Na_2CO_3) are found to form on the banks of certain saline lakes in Egypt. But the question is, how sodium carbonate is able to crystallize on the banks of these lakes ? C.L. Bertholet (1799) explained the above phenomenon by attributing large amount of NaCl present in lake water which forces the following reaction to occur.

$$2NaCl + CaCO_3 = CaCl_2 + Na_2CO_3$$

Hence the reverse reaction also takes place depending on the environment i.e., concentration. He concluded that **"the chemical activity of a substance depends on the force of its affinity and upon the mass which is present in a given volume."**

It is observed that a large number of reactions do not go to completion. Thus ethyl alcohol reacts with glacial acetic acid to form ethyl acetate and water. But study of the reaction shows that even after a considerable period of time the system contains both the reactants and the products.

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

It is further observed that at a given temperature ⅔rd of the reactants appears as the products while ⅓rd of the reactants remains unchanged. Again when equimolar quantities of ethyl acetate and water are mixed, reverse reaction starts and continues until ⅓rd of ester and water is converted into acetic acid and alcohol. This shows that the above reaction is reversible and hence is never completed.

10.2. Reversible reaction.

Whenever a chemical reaction is allowed to carry out under a given condition, it is observed that the products as soon as formed, start reacting to form the reactants again. These two opposite reactions take place ***simultaneously.*** Hence they do not go to completion.

(i) Some PCl_5 is taken in a closed vessel and is heated to a certain temperature. PCl_5 decomposes into PCl_3 and Cl_2. Even if the temperature is increased PCl_5 is not completely decomposed into its products namely PCl_3 and Cl_2. Analysis of the products shows the presence of PCl_3, Cl_2 and undissociated PCl_5. Similarly if now equimolar quantities of PCl_3 and Cl_2 are heated in the same closed vessel, the products will not be PCl_5 quantitatively but contains PCl_5 along with uncombined PCl_3 and Cl_2 even if the reactants are heated for a prolonged period of time. In either of the two reactions, always a mixture consisting of PCl_5, PCl_3 and Cl_2 is obtained. The rate at which PCl_5 dissociates into PCl_3 and Cl_2 is the same as PCl_3 and Cl_2 recombine to revert back into PCl_5.

$$PCl_5 \rightarrow PCl_3 + Cl_2$$
$$PCl_3 + Cl_2 \rightarrow PCl_5$$

Thus we conclude that chemical reactions do not proceed to completion. This means that a mixture of reactants is not entirely converted into products, instead, after sometime, the concentrations of the reactants no longer decrease. At this point the reaction system consists of a mixture of reactants and products. When such a condition is attained, the system is said to be in a state of ***chemical equilibrium.***

(ii) Another example of a reversible reaction is provided by the formation of steam when water is heated in a closed iron vessel. The steam attacks iron to form ferroso-ferric oxide and hydrogen, the latter reacts with ferroso-ferric oxide to form iron and steam. The reactions never proceed to completion.

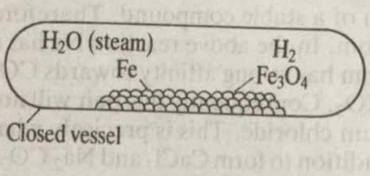


Fig 10·1

Two reactions proceed simultaneously

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \text{ [Forward reaction]}$$
$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O \text{ [Backward reaction]}$$

Every reversible reaction culminates into a state of equilibrium when the rate of forward reaction is equal to the rate of backward reaction. In the above reaction the rate at which iron and steam combine to form ferroso-ferric oxide and hydrogen, is the same as the rate in which hydrogen reacts with ferroso-ferric oxide to form iron and steam.

Definition : *A reaction is said to be reversible when the reactants combine among themselves to form the products which as soon as formed, start reacting among* *themselves to reform the reactants and attain a state of equilibrium depending upon the concentration and other conditions of the components of reaction. Thus in a reversible reaction there is a natural tendency to approach a state when the speed of the forward reaction becomes equal to the speed of the reverse reaction.*

10.3. Chemical equilibrium.

When an equimolecular mixture of hydrogen and iodine is heated at 440°C in a closed vessel for about two hours or so, 80% hydrogen iodide is formed.

$$H_2 + I_2 = 2HI$$

remaining 20% being mixture of H_2 and I_2.

Now in a similar closed vessel pure HI is kept at 440°C. After a period of about two hours it is observed that 80% HI remains as undissociated and only 20% dissociate as H_2 and I_2.

$$H_2 + I_2 \rightleftharpoons 2HI$$

Initially the concentration of H_2 and I_2 was maximum but with the interval of time the forward reaction proceeds but the concentration of HI remains comparatively low. The two reactions represent two directions of a reversible reaction.

$$H_2 + I_2 \rightarrow 2HI$$
$$2HI \rightarrow H_2 + I_2$$

As soon as HI is formed in the first reaction, it starts decomposing into H_2 and I_2. As time is elapsed, the concentration of H_2 and I_2 decreases and the concentration of HI is increased. Consequently the rate of forward reaction decreases and the rate of backward reaction increases. The process continues and the decrease of the rate of the forward reaction and the increase of the rate of the backward reaction reaches a point when the speed of the forward reaction becomes equal to the speed of the backward reaction. The system is then said to attain equilibrium and no further change of concentration of the reactants H_2 and I_2 and the product HI will take place. Not only in chemical reaction but also in physical process equilibrium is a common phenomenon. For examples in a closed vessel, the vapour above a liquid achieves an equilibrium with the liquid phase. The rate at which molecules escape from the liquid to the gas phase is equal to the rate at which molecules of the gas phase strike the surface and become part of the liquid.

Definition : *Chemical equilibrium is defined as a state when the velocity or speed of the forward reaction is the same as the velocity or speed of the backward reaction of a reversible reaction.*

The following points are to be noted for characterising a state of equilibrium.

(a) The rates of forward and backward reaction are the same and the two reactions act in opposite direction.

(b) At any instant there is no change in the ratio of the masses of the products and the reactants. Thus it appears as if the reaction has been stopped.

(c) Change of temperature, pressure or concentration alter either the rate of forward or backward reaction. Hence there is change of point of chemical equilibrium.

(d) The reaction does not stop at all i.e., the system is not static. On the contrary reaction proceeds in either direction continuously. The equilibrium is a dynamic one—a state where chemical changes are taking place on the molecular level i.e., the number of molecules undergoing forward reaction is the same as the number of molecules undergoing the reverse reaction so that the rates of the two reactions remain constant.

- **Dynamic nature of chemical equilibrium :**

Whenever a reversible reaction reaches equilibrium it appears to be static in nature as if the reaction is ceased, because the concentrations of neither the reactants nor the products undergo any appreciable change even after a long time of interval unless it is acted upon by the environment i.e., change of temperature, pressure, concentration etc. But actually this is not the fact i.e., the system is not static. The equilibrium is a ***dynamic one***—the rate of the forward reaction being just equalled by the rate of the backward one. In fact chemical change is constantly taking place in either of the directions.

When water is heated in a closed iron vessel, steam starts reaction at first with red hot iron at a certain speed.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

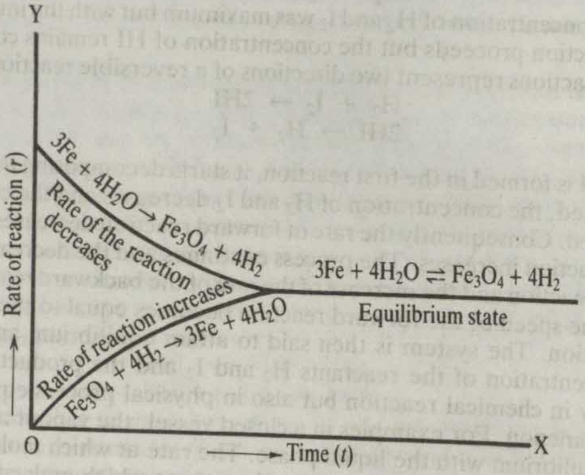


Fig 10.2 : Graph showing the rate of forward, backward and equilibrium state with the change of time.

But as the time passes the concentration of iron and steam diminishes and the rate of the forward reaction decreases. Again initially the concentration of Fe_3O_4 and H_2 was zero. But as the reaction proceeds towards right, the concentration of Fe_3O_4 and H_2 starts increasing and the rate of backward reaction i.e., formation of iron and steam increases. $Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$

Thus in these two opposite reactions the speed of the forward reaction decreases while that of reverse reaction gradually increases and finally a condition is reached when the speed of the forward reaction becomes equal to the speed of the backward reaction. Both the reactions, forward and backward proceeds simultaneously with the same rate. The reactions do not stop at all. The system has then attained equilibrium and concentrations of neither the reactants nor the products alter at this point. The above graph (Fig 10.2) shows how the chemical equilibrium of the above reversible reaction has been reached by plotting the simultaneous decrease of the rate of forward reaction and increase of backward reaction against time. At this state (chemical equilibrium) no chemical transformation will be observed and the reaction will appear to be completely stopped because the concentrations of neither the reactants nor the products show any change. *But inspite of being at equilibrium, the reactants and the products do not become inactive.* On the contrary as many molecules of iron and steam combine to form Fe_3O_4 and hydrogen molecules at a given time of interval, the same number of Fe_3O_4 and H_2 molecules undergo chemical transformation to form Fe and steam molecules or *the rate at which iron and steam undergo to form Fe_3O_4 and H_2 is equal to the rate of formation of iron and steam by the combination Fe_3O_4 and H_2. This is the cause of equilibrium. Since at equilibrium the formation of the products from the reactants and the formation of the reactants from the products continue simultaneously, chemical equilibrium is called dynamic equilibrium—static equilibrium is a hypothetical case— a myth.*

10.4. Characteristics of chemical equilibrium.

A close scrutiny on the study of different aspects of chemical equilibrium shows the following important characteristics.

(i) ***At a given temperature when a reversible reaction reaches equlibrium state, it will remain undisturbed unless the reactants undergo some equivalent changes.*** Under this condition the concentrations of the reactants and products remain fixed. However the change of temperature affects the equilibrium.

(ii) ***Equilibrium can be attained from either side of the reaction.*** Thus at a given temperature if some reactants are allowed to attain equilibrium to form desired products and the concentrations of the equilibrium products are measured, then in another experiment when these products are allowed to react to attain equilibrium, the concentrations of all the components at equlibrium are found to be same as before provided the temperature remains constant.

When electric spark is applied to pure NH_3 gas, it is dissociated to the extent of 93%

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Again pure nitrogen and pure hydrogen in the ratio of 1 : 3 by volume, are allowed to combine under specific condition, only 7% of the gas mixture are converted to form NH_3 and the remaining 93% are left unreacted.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Thus equilibrium can be reached either from R.H.S. or from L.H.S. of the reaction i.e., *whether we start with reactants or products, same equilibrium state will be reached.* This can be shown by considering the following reaction.

$$\underset{\text{Colourless}}{N_2O_4\,(s)} = \underset{\text{Brown}}{2NO_2\,(g)}$$

Experiment : Under the same pressure pure NO_2 gas is filled in two identical glass bulbs A and B of same volume. The bulb (A) is immersed in ice water while the other

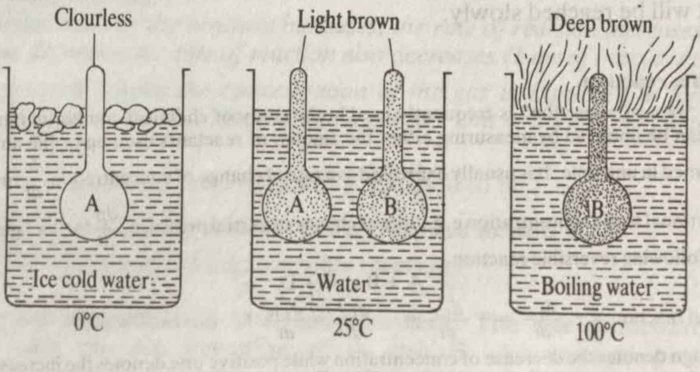


Fig 10·3

one (B) in hot water (Fig 10.3). After some time it will be observed that the gas in bulb (A) becomes colourless while that in bulb (B) becomes reddish brown. This proves that (A) contains N_2O_4 while the bulb (B) contains NO_2.

Now both the 2 bulbs are immersed in water kept at 25°C. The colour of both the bulbs changes after some time. The bulb (A) becomes faintly brown colour while that of (B) diminishes the intensity of colour and becomes light brown. The colour of gas in both the 2 bulbs will be identical. This is an example of attainment of equilibrium from either side of a reversible reaction which can be observed visually.

(iii) ***Neither the forward nor the backward reaction in equilibrium state of a reversible reaction is complete.*** The above statement signifies that neither the reactants nor the products are fully consumed at the equilibrium point. Thus in the following reaction : $A + B \rightleftharpoons C + D$, the rate of consumption of both A and B leading to the formation of C and D is the same as the rate of reformation of A and B from C and D at equilibrium state. As a result of this, A and B are never converted into C and D quantitatively. At this point, a mixture of A, B, C and D is found to contain in the reaction vessel. When the above reaction reaches equilibrium the equilibrium constant K_c at a fixed temperature is given by

$$K_c = \frac{[C]\,[D]}{[A]\,[B]}$$

If we assume any one of the above is completely used up during the course of reaction, then K is either 0 or $\propto$. This does not carry any sense or this state is never attained at equilibrium. Hence a reversible reaction is never completed.

(iv) ***Equilibrium reactions are studied in a closed vessel.*** This is very important, since in an open vessel the products may escape and the reversible reaction becomes an irreversible one.

(v) ***At constant temperature there is a tendency of all reversible reactions to attain equilibrium in a closed system. But if the equilibrium is subjected to a stress such as changes in temperature, pressure, concentration etc., the system adjusts itself in such a way so as to uhdo the action of the applied stress (Le-Chatelier's principle) and re-attain the equilibrium.***

(vi) ***At equilibrium the rate of forward reaction is the same as that of the backward one.***

(vii) ***A chemical equilibrium is a dynamic one—not static.*** The reaction does not stop.

(viii) ***The time of attainment of chemical equilibrium is different in different reactions.*** If the rates of the reactions (both forward and backward) are high, equilibrium will be attained quickly. On the other hand if the rates of the reactions are low, it will be reached slowly.

- **Rate of a reaction.**

The term "rate of a reaction" is frequently used in the study of chemical equilibrium and chemical kinetics. If can be obtained by measuring either the amount of reactants used up or the amount of the products formed in unit time. It is usually expressed as a rate of change of concentration $\frac{dc}{dt}$ or any property proportional to the concentration e.g., rate of change of partial pressure $\frac{dp}{dt}$ for a gas reaction. Thus in the following reversible reaction.

$$A + B \rightleftharpoons C + D$$

$$\text{Rate of reaction} = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} = \frac{dc_C}{dt} = \frac{dc_D}{dt}$$

Negative sign denotes the decrease of concentration while positive one denotes the increase of concentration with the increase of time. Thus if a volume of 1600 ml of Argon gas be passed through a 100 ml hot tube in 300 sec, the rate of flow of gas is $\frac{1600}{300} = 400 \text{ ml sec}^{-1}$

[See chapter on chemical kinetics vol II]

10.5. Law of mass action.

The effect of the concentration of the reactants on the rate of a chemical reaction is governed by the Law of mass action which was put forward in 1867 by *C.M. Guldberg* and *P. Waage*. The Law states :

- *The rate of a chemical reaction at any instant at a given temperature is proportional to the active mass of each of the reacting substances present in the system at that instant.*

The Law of mass action is applicable to both homogeneous and heterogeneous equilibria.

Active mass : *By the term active mass we generally mean the molar concentration of the reactants i.e., gram-moles per litre or moles per litre.*

(i) The active mass of a substance is only equal to its molar concentration if there is no interaction or interference among the molecules in solution. If there is enough ionic interference i.e., when the solution is concentrated then :—

Active mass = Molar concentration × Activity co-efficient

In very dilute solution, ionic interference is so small that it may be regarded as negligible. In that case activity co-efficient approaches 1 and Active mass = Molar concentration. In our discussion of chemical equilibrium activity co-efficient will be regarded as unity so that Active mass = Molar concentration.

Let x g of a reactant A is present in V litre of solution. Let M be the gram-molecular weight of A

V litres of the solution contain $\frac{x}{M}$ moles of A

1 " " " " " $\frac{x}{M \times V}$ " "

$$\therefore \text{ Active mass of A} = [\text{A}] = \frac{x}{M \times V}$$

$$= \frac{\text{Weight in gram of the substance}}{\text{Volume of the solution in litre} \times \text{Mol. weight of the substance}}$$

Thus if 20 g of NaOH be dissolved in 5 litre of solution then the active mass of NaOH.

$$[\text{NaOH}] = \frac{20}{5 \times 40} = 0{\cdot}1 \text{ moles litre}^{-1}$$

If the active mass of the reactant increases, the rate of reaction increases and if the active mass decreases the rate of reaction also decreases (Law of mass action).

(ii) *In gaseous system the concentration of the gas is expressed in term of their partial pressures since partial pressure of a gas per unit volume is proportional to its moles.*

(iii) The active mass of solid reactants is assumed to be 1.

- **Mathematical expression of law of mass action :**

Let us consider the following reversible reaction—

$$\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$$

Initially the concentration of C and D is zero. The rate of forward reaction depends upon the concentration of A and B. As reaction proceeds the concentration of C and D increases and that of A and B decreases. The reverse reaction starts as soon as C and D are formed.

The rate of the backward reaction depends upon the concentration of both C and D. A time comes when the rate of forward reaction is equal to the rate of backward reaction—a dynamic equilibrium sets in at a given temperature.

Let at equilibrium the concentrations of A, B, C and D be denoted by [A], [B], [C] and [D] respectively. Let r_1 be the rate of the forward reaction $A + B \rightarrow C + D$ and r_2 be the rate of the backward reaction $C + D \rightarrow A + B$. Hence according to the law of mass action.

$$r_1 \propto [A]\,[B]$$

$$\text{or, } r_1 = K_1\,[A]\,[B] \ldots\ldots\ldots\ldots\ldots (1)$$

where K_1 is a constant known as velocity constant or rate constant for the forward reaction.

Similarly $r_2 \propto [C]\,[D]$

$$\text{or, } r_2 = K_2\,[C]\,[D] \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where K_2 is a constant known as velocity constant or rate constant for the backward reaction.

At equilibrium $r_1 = r_2$

$$\text{or, } K_1\,[A]\,[B] = K_2\,[C]\,[D]$$

$$\text{or, } \frac{K_1}{K_2} = \frac{[C]\,[D]}{[A]\,[B]}$$

Now let $\dfrac{K_1}{K_2} = K$

$$\therefore\ K = \frac{[C]\,[D]}{[A]\,[B]}$$

Since K_1 and K_2 are constant hence K is also constant. K is called *equilibrium constant. It depends upon the temperature.*

Let us now consider the reaction—

$$2A \leftrightharpoons 3C + 2D$$

The reaction can be written as $A + A \leftrightharpoons C + C + C + D + D$

Rate of forward reaction—

$$r_1 \propto [A]\,[A]$$

$$\text{or, } r_1 = K_1\,[A]\,[A]$$

$$\text{or, } r_1 = K_1\,[A]^2$$

Rate of backward reaction—

$$r_2 \propto [C]\,[C]\,[C]\,[D]\,[D]$$

$$\text{or, } r_2 = K_2\,[C]^3\,[D]^2$$

$$\text{or, } K_c = \frac{K_1}{K_2} = \frac{[C]^3\,[D]^2}{[A]^2}$$

The expression of equilibrium constant for a general equation of the type—

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D \text{ is}$$

$$K = \frac{[C]^\gamma\,[D]^\delta}{[A]^\alpha\,[B]^\beta}$$

10.6. Equilibrium constant.

Equilibrium constant (K) of a reversible reaction is the ratio of the rate constants for the forward and backward reaction. In the words, it is the ratio of concentration of the products and the reactants, each being raised to a power indicating the number of molecules of the substances taking part in the reaction.

Depending upon the type of reaction, K is given different symbols e.g., K_c, K_p, and K_x although their physical significance remains the same.

(i) $\boldsymbol{K_c}$: When the reaction is considered in *aqueous medium* and the concentrations of the reactants and the products are expressed in *moles per litre*, the equilibrium constant (K) is written as K_c

$$K_c = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$$

(ii) $\boldsymbol{K_p}$: When we consider a gaseous reaction the equilibrium constant is replaced by K_p.

Here the concentrations of the gaseous reactants and products are replaced by their *partial pressures* since active mass of a gas is directly proportional to its partial pressure. In that case the expression for equilibrium constant is

$$K_p = \frac{(P_C)^\gamma \times (P_D)^\delta}{(P_A)^\alpha \times (P_B)^\beta}$$

Where P_A, P_B, P_C and P_D are the partial pressures of the gaseous components A, B, C and D respectively.

(iii) $\boldsymbol{K_x}$: If the concentrations of the reactants and the products are expressed in *mole fraction* instead of moles per litre in an aqueous solution, the equilibrium constant (K) is written as

$$K_x = \frac{(x_C)^\gamma \times (x_D)^\delta}{(x_A)^\alpha \times (x_B)^\beta}$$

Where x_A, x_B, x_C and x_D are the mole fractions of A, B, C and D respectively of the reversible reaction $\alpha A + \beta B \leftrightharpoons \gamma C + \delta D$

10.7. Relation between K_p and K_c.

Let us consider a general reversible reaction

$$\alpha A + \beta B \leftrightharpoons \gamma C + \delta D$$

Let the concentrations of A, B, C and D in moles per litre be represented as [A], [B], [C] and [D] respectively.

$$K_c = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$$

Again let P_A, P_B, P_C and P_D be the partial pressures of the gaseous component A, B, C and D respectively.

$$K_p = \frac{(P_C)^\gamma \times (P_D)^\delta}{(P_A)^\alpha \times (P_B)^\beta}$$

For 1 mole of an ideal gas, $PV = RT$

For n moles of an ideal gas, $PV = nRT$ or, $P = \frac{n}{V}RT$

or, $P = cRT$ where $c = \frac{n}{V}$ = concentration in mole/litre.

Substituting for the components A, B, C and D,

$$P_A = [A]RT, \quad P_B = [B]RT, \quad P_C = [C]RT, \quad P_D = [D]RT$$

Substituting the aboves values of P_A, P_B, P_C and P_D in the expression for K_p

$$K_p = \frac{[C]^\gamma [RT]^\gamma [D]^\delta [RT]^\delta}{[A]^\alpha [RT]^\alpha [B]^\beta [RT]^\beta}$$

$$\begin{aligned}
K_p &= \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta} \cdot \frac{[RT]^\gamma [RT]^\delta}{[RT]^\alpha [RT]^\beta} \\
&= K_c \cdot \frac{[RT]^{\gamma+\delta}}{[RT]^{\alpha+\beta}} \\
&= K_c \quad [RT]^{(\gamma+\delta)-(\alpha+\beta)} \\
K_p &= K_c \quad [RT]^{\Delta n}
\end{aligned}$$

where $\Delta n = (\gamma + \delta) - (\alpha + \beta)$

= total number of molecules of the product − total number of molecules of the reactants

(i) When $\Delta n = 0 \quad K_p = K_c\,[RT]^0 \quad or, \quad K_p = K_c$

Examples :

$$\underset{\substack{(g)\\ \text{1 mole}}}{H_2} + \underset{\substack{(g)\\ \text{1 mole}}}{I_2} \leftrightharpoons \underset{\substack{(g)\\ \text{2 moles}}}{2HI}$$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2}).(P_{I_2})} = \frac{[HI]^2[RT]^2}{[H_2][I_2][RT]^2} = \frac{[HI]^2}{[H_2\}[I_2]} = K_c$$

Other examples :

$$\underset{(g)}{N_2} + \underset{(g)}{O_2} \leftrightharpoons \underset{(g)}{2NO}$$

$$\underset{(g)}{CO} + \underset{(g)}{H_2O} \leftrightharpoons \underset{(g)}{H_2} + \underset{(g)}{CO_2}$$

$$\underset{(g)}{CO} + \underset{(g)}{NO_2} \leftrightharpoons \underset{(g)}{CO_2} + \underset{(g)}{NO}$$

(ii) When $\Delta n \neq 0, K_p \neq K_c$

Example : $N_2 + 3H_2 \leftrightharpoons 2NH_3$

$\Delta n = 2 - 4 = -2$

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2}) \cdot (P_{H_2})^3} = \frac{[NH_3]^2[RT]^2}{[N_2][H_2]^3[RT]^4} = \frac{[NH_3]^2}{[N_2][H_2]^3} \cdot \frac{1}{[RT]^2}$$

$K_p = K_c[RT]^{-2}$ Hence, $K_p \neq K_c$

Other examples of this type :

$$\underset{(g)}{2SO_2} + \underset{(g)}{O_2} \leftrightharpoons \underset{(g)}{2SO_3}$$

$$\underset{(g)}{PCl_5} \leftrightharpoons \underset{(g)}{PCl_3} + \underset{(g)}{Cl_2}$$

$$\underset{(g)}{2H_2} + \underset{(g)}{O_2} \leftrightharpoons \underset{(g)}{2H_2O}$$

$$\underset{(g)}{4HCl} + \underset{(g)}{O_2} \leftrightharpoons \underset{(g)}{2H_2O} + \underset{(g)}{2Cl_2}$$

$$\underset{(g)}{2CO} + \underset{(g)}{O_2} \leftrightharpoons \underset{(g)}{2CO_2}$$

- **K_p of the reaction : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at absolute zero.**

$$\underset{\text{1 mole}}{N_2(g)} + \underset{\text{1 mole}}{O_2(g)} \rightleftharpoons \underset{\text{2 mole}}{2NO(g)}$$

Since $K_p = K_c[RT]^{\Delta n}$
At absolute zero i.e., at 0 K, T = 0
So, $K_p = K_c\ [R \times 0]^{\Delta n}$
or, K_p is zero.

10.8. Relation between K_p and K_x.

We know partial pressure of a gas (p) = Mole fraction x × Total pressure P

$$\text{or, } p = XP$$

For the reaction $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$

$$K_p = \frac{(p_C)^\gamma (p_D)^\delta}{(p_A)^\alpha (p_B)^\beta}$$

$$= \frac{(x_C)^\gamma (P)^\gamma (x_D)^\delta (P)^\delta}{(x_A)^\alpha (P)^\alpha (x_B)^\beta (P)^\beta}$$

$$\text{or, } K_p = \frac{(x_C)^\gamma (x_D)^\delta}{(x_A)^\alpha (x_B)^\beta} \cdot \frac{(P)^{\gamma+\delta}}{(P)^{\alpha+\beta}}$$

$$= K_x \,.\, P^{(\gamma+\delta)-(\alpha+\beta)} \qquad \text{Since } K_x = \frac{(x_C)^\gamma (x_D)^\delta}{(x_A)^\alpha (x_B)^\beta}$$

$$= K_x \,.\, P^{\Delta n}$$

$$\text{or, } \boldsymbol{K_p = K_x \,.\, P^{\Delta n}}$$

Similarly relation between K_c and C_x can be evaluated as follows :—
We know, $K_p = K_c\,(RT)^{\Delta n}$
again, $K_p = K_x \,.\, P^{\Delta n}$

$$\therefore\ K_x \,.\, P^{\Delta n} = K_c\,(RT)^{\Delta n}$$

$$K_x = K_c \,.\, \frac{[RT]^{\Delta n}}{P^{\Delta n}}$$

$$= K_c \left(\frac{RT}{P}\right)^{\Delta n} = K_c V^{\Delta n}$$

Where V = Partial molar volume of the gas in the given mixture.
However when $\Delta n = 0$, $\boldsymbol{K_p = K_c = K_x}$

10.9. Characteristics of equilibrium constant (*K*).

(i) *The equilibrium constant of all reversible reactions at constant temperature is constant.* However, *for exothermic process the equilibrium constant decreases with the rise of temperature while for endothermic process it increases.*

Relation between equilibrium constant and temperature :
If K_1, K_2 be the equilibrium constants of a reaction at temperatures T_1 and T_2 (in absolute scale) and ΔH = Heat of reaction or Enthalpy—

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\text{or, } \log \frac{K_2}{K_1} = \frac{\Delta H}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

(ii) *At constant temperature, the numerical value of K does not depend upon the concentration i.e. actual amount of the reactants and products. Whatever may be their concentration, the value of K remains constant, provided temperature remains constant since K is a ratio of their concentration.*

Again the active mass or the concentration of the solid is assumed to be unity and the term does not appear in the equilibrium constant expression.

$$C(g) + CO_2(g) \rightleftharpoons 2CO(g)$$

$$K_c = \frac{[CO]^2}{[CO_2]} \quad \text{or,} \quad K_p = \frac{(P_{CO})^2}{(P_{CO_2})}$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$\text{here, } K_p = P_{CO_2} \quad \text{and } K_c = [CO_2]$$

(iii) *The equilibrium constant of a forward reaction is reciprocal of its backward reaction.*

Examples :

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$K_f = \text{Eq. constant for forward reaction} = \frac{[NO]^2}{[N_2][O_2]}$$

In the backward reaction $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

$$K_b = \text{Eq. constant for backward reaction} = \frac{[N_2][O_2]}{[NO]^2}$$

$$\text{or,} \quad K_f = \frac{1}{K_b}$$

(iv) *The equilibrium constant may have unit or may not have any unit (pure number) in different reactions.*

If $\triangle n = 0$, the numerical value K is a pure number.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{\text{mole}}{\text{litre}}\right)^2}{\frac{\text{mole}}{\text{litre}} \times \frac{\text{mole}}{\text{litre}}}$$

However if $\triangle n \neq 0$, K must have an unit

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{\text{mole}}{\text{litre}}\right)^2}{\frac{\text{mole}}{\text{litre}} \times \left(\frac{\text{mole}}{\text{litre}}\right)^3} = \frac{1}{\left(\frac{\text{mole}}{\text{litre}}\right)^2} = \left(\frac{\text{litre}}{\text{mole}}\right)^2$$

(v) *The numerical value of equilibrium constant depends upon the stoichiometry of the reversible reaction.*

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$K_1 = \frac{[HI]^2}{[H_2][I_2]}$$

Again the above reaction can be represented as follows :—

$$\tfrac{1}{2} H_2 + \tfrac{1}{2} I_2 \rightleftharpoons HI$$

$$K_2 = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} \text{ or, } K_2 = \sqrt{K_1}$$

(vi) *The position of equilibrium in a reversible reaction is not affected by a catalyst.*

Since a catalyst accelerates the forward and the backward reaction equally, K remains constant.

$$K = \frac{K_1}{K_2}$$

K_1 and K_2 are the velocity or rate constants for the forward and backward reaction respectively.

10.10. Types of chemical equilibrium.

Two types of chemical equilibria are known.

(a) **Homogeneous equilibrium :** If all the constituent participants of a reversible reaction are in one phase—liquid or gas, the system is called *Homogeneous system* and the equilibrium in such system is called Homogeneous equilibrium.

Example : $$2SO_2\,(g) + O_2\,(g) \leftrightharpoons 2SO_3\,(g)$$

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \leftrightharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

(b) **Heterogeneous equilibrium :** A system is said to a Heterogeneous one, if the phase of any one component is different from the other. The equilibrium in such system is called Heterogeneous equilibrium.

Example : $$C\,(s) + O_2\,(g) \leftrightharpoons CO_2\,(g)$$

$$CaCO_3\,(s) \leftrightharpoons CaO\,(s) + CO_2\,(g)$$

Law of mass action is applicable to both homogeneous and heterogeneous equilibria.

10.11. Importance of equilibrium constant.

The knowledge of the equilibrium constant of a reversible reaction especially its numerical magnitude is a great importance to chemists and chemical engineers.

(1) The numerical value of K indicates the position of equilibrium i.e., it shows how far the reaction proceeds towards completion.

$$A + B \leftrightharpoons C + D$$

$$K_c = \frac{[C][D]}{[A][B]}$$

(i) A low value of K_c ($K_c < 1$) indicates that [C] and [D] are small compared to [A] and [B] i.e., back reaction predominates. The yield of C and D is low. Hence it can be said that the backward reaction is near the completion.

(ii) A high value of K_c ($K_c > 1$) shows that most of A and B combine to form large amount of C and D i.e., [C] and [D] are large compared to [A] and [B] i.e., the forward reaction predominates. Thus in the following reaction—

$$2FeCl_3 + SnCl_2 \leftrightharpoons SnCl_4 + 2FeCl_2$$

$$K_c = 1{\cdot}00 \times 10^{21}$$

The high numerical value of K_c shows that the forward reaction practically goes to completion. This explain why Fe^{+++} and Sn^{++} ions cannot reside side by side in an aqueous medium.

(iii) If $K_c = 1$, then [C] [D] = [A] [B] or in other wards 50% of the reactants have been consumed to form the products.

Thus the numerical value of K of a reaction is profitably utilised in the industrial manufacture of the products.

(2) K indicates how the equilibrium shifts if the concentration changes. Thus if

[A] is changed by adding A from outside, the equilibrium shifts towards the right so that [C] and [D] increases but K_c remains constant.

Again if the value of K_c and the initial concentration of the reactants are known then the concentrations of both the reactants and the products can be evaluated when equilibrium is reached.

Example :

Calculate the concentrations of H_2O, CO, H_2 and CO_2 at equilibrium for the following reaction when 1 mole of H_2O and 1 mole of CO are allowed to react in a five litre flask ($K_c = 0.49$).

$$H_2O\,(g) + CO\,(g) \leftrightharpoons H_2\,(g) + CO_2\,(g)$$

Ans :

$$\begin{array}{lcccc} & H_2O\,(g)\ + & CO(g)\ \leftrightharpoons & H_2\,(g)\ + & CO_2\,(g) \\ \text{Initial} & 1\text{ mole} & 1\text{ mole} & 0\text{ mole} & 0\text{ mole} \\ \text{At equilibrium} & 1-x & 1-x & x & x \end{array}$$

x moles of H_2 and x moles of CO_2 are formed at equilibrium

∴ Concentrations of H_2O, CO, H_2 and CO_2 in mole/litre are $\frac{1-x}{5}$, $\frac{1-x}{5}$, $\frac{x}{5}$, $\frac{x}{5}$ respectively.

$$K_c = \frac{[H_2]\,[CO_2]}{[H_2O]\,[CO]}$$

$$= \frac{\frac{x}{5} \times \frac{x}{5}}{\frac{1-x}{5} \times \frac{1-x}{5}}$$

$$\text{or, } 0.49 = \frac{\frac{x}{5} \times \frac{x}{5}}{\frac{1-x}{5} \times \frac{1-x}{5}} \quad \text{or, } x = 0.412$$

At Equilibrium :

Number of moles of $H_2O = (1-0.412) = 0.588$
" " " " " $CO = (1-0.412) = 0.588$
" " " " " $H_2 = \quad 0.412 \quad = 0.412$
" " " " " $CO_2 = \quad 0.412 \quad = 0.412$

(3) *A knowledge of K shows the shift of equilibrium by change of pressure or concentration of the reactants or the products.*

Example : $N_2O_4 \leftrightharpoons 2NO_2$

Let a mole of N_2O_4 is heated in a flask of volume V litre. At equilibrium let x moles of NO_2 is formed.

$$\begin{array}{lcc} & N_2O_4 & \leftrightharpoons\ 2NO_2 \\ \text{Initial mole} & a & 0 \\ \text{Equilibrium mole} & a-x & 2x \\ \text{Concentration at equilibrium in mole/litre} & \frac{a-x}{V} & \frac{2x}{V} \end{array}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{2x}{V}\right)^2}{\frac{a-x}{V}} \qquad \text{or, } K_c = \frac{4x^2}{(a-x)\,V}$$

(i) **Influence of pressure :**

In the above expression V appears in the denominator. $[P \propto \frac{1}{V}]$. Hence V will decrease on increase of pressure. Since K_c is constant at constant temperature, decrease of V decreases x. Thus if pressure is increased, the dissociation of N_2O_4 must diminish, on the other hand if pressure is decreased yield of NO_2 will increase.

(ii) **Addition of NO_2 :**

Keeping the volume of the flask and the temperature constant, if some NO_2 gas is introduced into the flask $[NO_2]$ will increase. Since K_c is constant at constant temperature, the equilibrium will move in the opposite direction. The degree of dissociation of N_2O_4 will decrease or the yield of the product will diminish.

(4) K also allows us to predict the direction in which a reversible reaction will proceed to achieve equilibrium and to calculate the concentrations of the reactants and products once equilibrium has been reached.

10.12. Applications of Law of Mass action—Determination of equilibrium constant of a few reactions.

(1) **Synthesis of HI from hydrogen and iodine :**

	H_2 +	I_2	$\leftrightharpoons 2HI$
Initial number of moles	a	b	0
Number of moles at equilibrium	$a-x$	$b-x$	$2x$

'a' moles of hydrogen is allowed to react with 'b' moles of iodine at the start. At equilibrium let x moles of hydrogen disappear, hence $2x$ moles of HI is formed at equilibrium. Let the reaction be carried out in a V litre flask.

$\therefore$ Total number of moles at equilibrium present in the system

$$= a - x + b - x + 2x = a + b$$

Mole fraction of H_2, I_2 and HI are

$$x_{H_2} = \frac{a-x}{(a+b)}, \quad x_{I_2} = \frac{b-x}{(a+b)}, \quad x_{HI} = \frac{2x}{(a+b)}$$

Let P be the total pressure of the system then their partial pressure are,

$$P_{H_2} = \frac{a-x}{a+b} \cdot P; \quad P_{I_2} = \frac{b-x}{a+b} \cdot P; \quad P_{HI} = \frac{2x}{a+b} \cdot P$$

Molar concentration at equilibrium,

$$[H_2] = \frac{a-x}{V}, \qquad [I_2] = \frac{b-x}{V}, \qquad [HI] = \frac{2x}{V}$$

Now,

$$K_p = \frac{(P_{HI})^2}{P_{H_2} \cdot P_{I_2}} = \frac{\left(\frac{2x}{a+b} \cdot P\right)^2}{\frac{a-x}{a+b} \cdot P \times \frac{b-x}{a+b} \cdot P} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_x = \frac{(x_{HI})^2}{x_{H_2} \times x_{I_2}} = \frac{\left(\frac{2x}{a+b}\right)^2}{\left(\frac{a-x}{a+b}\right)\left(\frac{b-x}{a+b}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

Thus, $K_p = K_c = K_x$
This is evident that in this reaction $\triangle n = 0$

(2) Esterification reaction :

$$CH_3COOH + C_2H_5OH \leftrightharpoons CH_3COOC_2H_5 + H_2O$$

Let us start with '*m*' moles of CH_3COOH and '*n*' moles of C_2H_5OH. At equilibrium *x* moles of acid disappear or *x* moles of acid reacts with *x* moles of alcohol to form *x* moles of ester and *x* moles of water.

	CH_3COOH +	C_2H_5OH ⇋	$CH_3COOC_2H_5$ +	H_2O
Number of moles at the start	m	n	0	0
Number of moles at equilibrium	$m-x$	$n-x$	x	x

Let the total volume of the reaction be *V* litre

$$[CH_3COOH] = \frac{m-x}{V} \text{ mole/litre.}$$

$$[C_2H_5OH] = \frac{n-x}{V} \text{ mole/litre.}$$

$$[CH_3COOC_2H_5] = \frac{x}{V} \text{ mole/litre.}$$

$$[H_2O] = \frac{x}{V} \text{ mole/litre.}$$

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$= \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{m-x}{V} \times \frac{n-x}{V}} = \frac{x_2}{(m-x)\,(n-x)}$$

The term *V* is present neither on the numerator nor on the denominator in the above expression. Hence equilibrium does not depend upon the total volume of the reaction mixture. '*m*' gram-moles of acid would yield same amount of ester whatever be the concentration of acid.

Total number of moles at equilibrium $m - x + n - x + x + x = m + n$
Let *p* be the total pressure at equilibrium.
Partial pressure = Mole fraction × Total pressure

$$p_{CH_3COOH} = \frac{m-x}{m+n} \cdot p$$

$$p_{C_2H_5OH} = \frac{n-x}{m+n} \cdot p$$

$$p_{CH_3COOC_2H_5} = \frac{x}{m+n} \cdot p$$

$$p_{H_2O} = \frac{x}{m+n} \cdot p$$

$$K_p = \frac{p_{CH_3COOC_2H_5} \times p_{H_2O}}{p_{CH_3COOH} \times p_{C_2H_5OH}}$$

$$= \frac{\frac{x}{m+n} \cdot p \times \frac{x}{m+n} \cdot p}{\frac{m-x}{m+n} \cdot p \times \frac{n-x}{m+n} \cdot p} = \frac{x^2}{(m-x)\,(n-x)}$$

Again, $$K_x = \frac{x_{CH_3COOC_2H_5} \times x_{H_2O}}{x_{CH_3COOH} \times x_{C_2H_5OH}}$$

where "x" denotes mole fraction

$$\text{or, } K_x = \frac{\dfrac{x}{m+n} \times \dfrac{x}{m+n}}{\dfrac{m-x}{m+n} \times \dfrac{n-x}{m+n}} = \frac{x^2}{(m-x)(n-x)}$$

Here also $K_p = K_c = K_x$. Since $\Delta n = 0$

(3) **Thermal dissociation of PCl_5 :**

This is a typical example of reaction where $\Delta n \neq 0$

$$PCl_5 \leftrightharpoons PCl_3 + Cl_2$$

Let 'a' moles of PCl_5 is heated in a flask of capacity V litre at pressure 'p' atmosphere. Let x moles of PCl_5 disappear i.e. x moles of Cl_2 and x moles of PCl_3 are formed.

	PCl_5	$\leftrightharpoons$	PCl_3	+	Cl_2
Initial number of moles	a		0		0
Number of moles at equilibrium	$a-x$		x		x

$\therefore$ Total number of moles at equilibrium $= a-x+x+x = a+x$

$$x_{PCl_5} = \frac{a-x}{a+x} \qquad x_{PCl_3} = \frac{x}{a+x} \qquad x_{Cl_5} = \frac{x}{a+x}$$

$$[PCl_5] = \frac{a-x}{V} \qquad [PCl_3] = \frac{x}{V} \qquad [Cl_2] = \frac{x}{V}$$

$$p_{PCl_5} = \frac{a-x}{a+x} \cdot p \qquad p_{PCl_3} = \frac{x}{a+x} \cdot p \qquad p_{Cl_2} = \frac{x}{a+x} \cdot p$$

$$K_x = \frac{x_{PCl_3} \times x_{Cl_2}}{x_{PCl_5}}$$

$$= \frac{\left(\dfrac{x}{a+x}\right)\left(\dfrac{x}{a+x}\right)}{\dfrac{a-x}{a+x}} = \frac{x^2}{(a-x)(a+x)} = \frac{x^2}{a^2-x^2}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

$$= \frac{\left(\dfrac{x}{a+x}\right) \cdot p \times \left(\dfrac{x}{a+x}\right) \cdot p}{\left(\dfrac{a-x}{a+x}\right) \cdot p} = \frac{x^2 \cdot p}{(a-x)(a+x)} = \frac{x^2 \cdot p}{a^2-x^2}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\left(\dfrac{x}{V}\right)\left(\dfrac{x}{V}\right)}{\dfrac{a-x}{V}} = \frac{x^2}{(a-x)\,V}$$

We know for n moles of an ideal gas $PV = nRT$

Here n = number of moles $= a+x$

$$V = \frac{(a+x)\,RT}{p}$$

$$\text{or, } K_c = \frac{x^2}{a-x} \times \frac{p}{(a+x)\,\mathrm{RT}} = \frac{x^2 \cdot p}{(a^2-x^2).\,\mathrm{RT}}$$

$$\text{Again } K_p = \frac{x^2 \cdot p}{a^2-x^2} \quad \text{or, } \frac{K_p}{K_c} = \mathrm{RT}$$

In this reaction $\Delta = 1$, putting $\Delta = 1$ in the equation—

$$K_p = K_c\,(\mathrm{RT})^{\Delta n}\; K_p = K_c \cdot \mathrm{RT} \quad \text{or, } \frac{K_p}{K_c} = \mathrm{RT}$$

$$\text{Again } K_x = \frac{x^2}{a^2-x^2}$$

Substituting this value in the expression,

$$K_p = \frac{x^2 \cdot p}{a^2-x^2} \quad K_p = K_x p \quad \text{or, } \frac{K_p}{K_x} = p$$

We know $K_p = K_x P^{\Delta n}$, Since $\Delta = 1 \therefore K_p = K_x p$

It is evident from the equation $K_c = \dfrac{x^2 \cdot p}{(a^2-x^2)\,\mathrm{RT}}$ the increase of pressure will decrease x at constant temperature. This means that if pressure is decreased, the dissociation of PCl_5 would increase $(x \propto \frac{1}{p})$.

(4) Dissociation of Ammonium carbamate :

The dissociation of solid ammonium carbamate produces three molecules of gases

$$NH_4COONH_2\,(s) \leftrightharpoons 2NH_3\,(g) + CO_2\,(g)$$

This is an example of heterogeneous equilibrium which consists of one solid and two gases. The total pressure 'p' at constant temperature is due to 2 moles of NH_3 and one mole of CO_2

$$\text{Partial pressure } P_{NH_3} = \frac{2}{3}p$$

$$P_{CO_2} = \frac{1}{3}p$$

$$K_p = (P_{NH_3})^2 \times P_{CO_2} = (2/3\,p)^2 \times 1/3\,p \quad = 4/27\,p^3$$

$$\mathbf{K_p = 4/27\,p^3}$$

10.13. Le Chatelier's Principle.

The influence of *temperature, pressure, concentration* etc., (i.e., *change of environment)* on the position of equilibrium in a reversible reaction can be qualitatively predicted by *the principle of Mobile equilibrium* developed independently by H. Le Chatelier (1885) and F. Braun (1886). Principle of Mobile equilibrium is commonly referred to as *Le Chatelier's principle* which states—

If a change occurs in one of the factors, such as temperature, pressure, concentration etc., under which a system is in equlibrium, the system will tend to adjust itself in such a manner so as to undo the effect of that change, as far as possible.

It may be noted that Le Chatelier's principle is of general applicability to all system in equilibrium including chemical reaction and physical process.

- **Effect of temperature :**

The shifting of equilibrium by change of temperature can be qualitatively predicted from Le Chatelier's principle. If the temperature of a system at equilibrium is increased, the equilibrium will be shifted in the direction in which heat is absorbed.

On the otherhand when temperature is decreased the equilibrium will be shifted in the direction where heat is evolved.

(i) Thus in the following exothermic reaction—

$$N_2 + 3H_2 \leftrightharpoons 2NH_3 \qquad \Delta H = -22.08 \text{ k cal}$$

If temperature is increased the equilibrium will be shifted from right to left and decrease in temperature will shift it from left to right. At high temperature the equilibrium mixture will contain less amount of ammonia but at low temperature more NH_3 will be present in the equilibrium mixture. *Thus when heat is applied to an equilibrium system which is exothermic in the forward direction, the equilibrium shifts in the reverse direction i.e., in the direction of the reactants.*

(ii) In the endothermic reaction

$$N_2 + O_2 \leftrightharpoons 2NO \quad \Delta H + 43.0 \text{ k cal}$$

If the temperature is increased, equilibrium will be shifted from left to right and decrease in temperature will shift the equilibrium from right to left. This explains why in Birkland-Eyde process in the manufacture of HNO_3, a mixture of N_2 and O_2 is subjected to an electric spark to get maximum yield of nitric oxide. Thus it can be concluded that (1) An exothermic reaction should be preferably conducted at low temperature for favourable yield of the products. (However rate of the reaction must be considered). (2) An endothermic reaction should be subjected to high temperature so as to get favourable yield of the product. If the temperature of an exothermic reaction is enhanced, the backward reaction sets in and the yield of the product is severely depressed.

- **Quantitative prediction :**

The effect of temperature on a reversible reaction, (both exothermic and endothermic) can be quantitatively evaluated from Vont Hoff's equation which is expressed as.

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

T = Temperature in absolute scale, R = Universal gas constant, K_p = Equilibrium constant, ΔH = Enthalpy or heat of reaction.

- **Exothermic reaction :**

For exothermic reaction ΔH is negative, Vant Hoff's equation becomes,

$$\frac{d \ln k_p}{dT} = \frac{-\Delta H}{RT^2}$$

$$\text{or, } \int d \ln K_p = -\frac{\Delta H}{R} \int \frac{dT}{T^2}$$

$$\text{or, } \ln K_p = \frac{\Delta H}{R} \cdot \frac{1}{T} + c$$

$$\text{or, } 2.303 \log K_p = \frac{\Delta H}{R} \cdot \frac{1}{T} + c$$

$$\log K_p = \frac{\Delta H}{2.303 R} \cdot \frac{1}{T} + c'$$

Since ΔH and R are constants $\log K_p \propto \frac{1}{T}$

Hence for exothermic reaction, decrease of temperature favours the forward reaction.

- **Endothermic reaction :** Here ΔH is positive

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

$$\text{or, } \int d \ln K_p = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

$$\text{or, } \ln K_p = -\frac{\Delta H}{R} \cdot \frac{1}{T} + c$$

$$\text{or, } \log K_p = -\frac{\Delta H}{2.303 R} \cdot \frac{1}{T} + c'$$

$$\text{or, } \log K_p \propto -\frac{1}{T} \qquad \text{or, } \log K \propto T$$

Since the value of ΔH is positive, the value of $-\frac{\Delta H}{RT}$ will be negative in the equation

$$\ln K_p = -\frac{\Delta H}{RT} + c$$

***If T* is increased, $-\frac{\Delta H}{RT}$ will be smaller so that *K* will increase. Increase in *T* therefore causes a shift of equilibrium from left to right for an endothermic reaction. Decrease in *T* causes a shift from right to left in $N_2 + O_2 \leftrightharpoons 2NO$, $\Delta H = 43$ k cal**

Hence all endothermic reactions should be conducted at high temperature to obtain maximum yield of the products.

• Effect of temperature in certain reactions :

Reversible reaction	'T' is increased	'T' is decreased
$2SO_2 + O_2 \leftrightharpoons$ $2SO_3 + 45$ k cal (Exothermic)	(a) The forward reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is exothermic. Increase of temperature will not favour the forward reaction hence the yield of SO_3 will decrease. (b) $2SO_3 \rightarrow 2SO_2 + O_2$ The reverse reaction is endothermic. Hence increase of temperature will favour the yield of SO_2 and O_2.	(a) The forward reaction being exothermic, will be favoured. Hence the yield of SO_3 will be increased when temperature is lowered. (b) $2SO_3 \rightarrow 2SO_2 + O_2$ The reverse reaction being endothermic, decrease of temperature will not favour the reaction. Thus the yield of SO_2 and O_2 will decrease.
$N_2 + O_2 \leftrightharpoons 2NO -$ 43·0 k cal (Endothermic)	(a) $N_2 + O_2 \rightarrow 2NO$ The forward reaction is endothermic. Hence increase of temperature will favour the forward reaction and the yield of NO will be enhanced. (b) $2NO \rightarrow N_2 + O_2$ The reverse reaction is exothermic. Increase of temperature will not favour the reaction. Hence yield of N_2 and O_2 will decrease.	(b) $N_2 + O_2 \rightarrow 2NO$ Decrease of temperature will not favour the abcve forward reaction. Hence on decreasing the temperature the yield of NO will be decreased. (b) $2NO \rightarrow N_2 + O_2$ Reverse reaction will be favoured when temperature is decreased. Hence at low temperature the yield of N_2 and O_2 will increase.

• Effect of Pressure :

(i) When the pressure on a system in equilibrium is increased, according to Le Chatelier's principle a change will take place in the system so that the additional pressure is relieved. This is possible if the equilibrium be shifted in the direction where the volume of the system decreases. Consequently, the increase of pressure will favour the reaction in the direction in which the reaction occurs with the decrease in volume i.e., decrease in the number of molecules present at equilibrium. (ii) On the other hand, decrease of pressure of the gas mixture at equilibrium will result in the shift in the direction of an increased number of molecules i.e., volume. (iii) If in a reaction $\Delta n = 0$ i.e., a reaction with no change in the number of molecules, change of pressure has no effect on the chemical equilibrium.

$$\underset{\text{1 vol}}{N_2} + \underset{\text{3 vol}}{3H_2} \leftrightharpoons \underset{\text{2 vol}}{2NH_3}$$

In the above reaction the total volume of the reactants = 4 and that of the products = 2. According to Le Chatelier's principle in a reversible reaction where products occupy smaller volume than the reactants (where $\Delta n = -ve$) the yield of the products is favoured at high pressure. In NH_3 synthesis by Haber's process a pressure as high as 200 atmosphere is employed.

If on the other hand pressure is diminished, equilibrium will be shifted towards increased volume i.e., towards left. Thus NH_3 will be dissociated at low pressure or the yield of NH_3 will be much depressed.

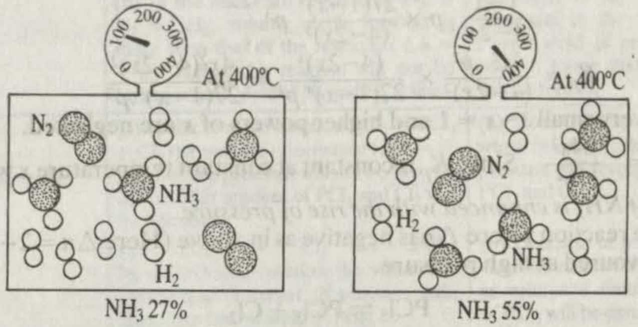


Fig 10.4. : The influence of pressure in the synthesis of ammonia.

Therefore, it can be fairly concluded that—

(i) In the gaseous reaction where Δn is negative i.e., volume is decreased, the yield of the products is favoured at high pressure. Increase in pressure, therefore, causes the equilibrium shift from left to right in the following reactions

$$N_2 + 3H_2 \leftrightharpoons 2NH_3$$
$$NH_3 + HCl \leftrightharpoons NH_4Cl$$
$$2SO_2 + O_2 \leftrightharpoons 2SO_3$$

(ii) In the gaseous reaction where Δn is positive i.e., volume is increased or products occupy larger volume than the reactants, the reaction is favoured at decreased pressure. Thus decrease in pressure causes the equilibrium to shift from left to right in the following reactions.

$$PCl_5 \leftrightharpoons PCl_3 + Cl_2$$
$$2NH_3 \leftrightharpoons N_2 + 3H_2$$
$$N_2O_4 \leftrightharpoons 2NO_2$$

(iii) If in a gaseous reaction $\Delta n = 0$ i.e., there is no change of volume, pressure has no effect on the equilibrium.

$$N_2 + O_2 \leftrightharpoons 2NO$$
$$H_2 + I_2 \leftrightharpoons 2HI$$

Effect of pressure on the gaseous reactions can be quantitatively shown as follows :—

(1)	N_2 +	$3H_2$ $\leftrightharpoons$	$2NH_3$
Number of moles at the start	1	3	0
Number of moles at equilibrium	$1-x$	$3(1-x)$	$2x$

$2x$ moles of NH_3 is formed at equilibrium. Let the pressure of the system at equilibrium be p.

Total number of moles of the gas mixture at equilibrium

$$= 1-x + 3-3x + 2x = 4 - 2x$$

Partial pressures of the components :—

$$p_{N_2} = \frac{1-x}{4-2x} \cdot p \ ; \qquad p_{H_2} = \frac{3(1-x)}{4-2x} \cdot p \quad p_{NH_3} = \frac{2x}{4-2x} \cdot p \ ;$$

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2}) \cdot (p_{H_2})^3}$$

Substituting the values of partial pressures

$$K_p = \frac{\frac{4x^2}{(4-2x)^2} \cdot p^2}{\frac{1-x}{4-2x} \cdot p \times \frac{27(1-x)^3}{(4-2x)^3} \cdot p^3}$$

$$K_p = \frac{4x^2 \cdot p^2}{(4-2x)^2} \times \frac{(4-2x)^4}{27(1-x)^4 \cdot p^4} = \frac{4x^2(4-2x)^2}{27(1-x)^4 \cdot p^2}$$

Since x is very small $1-x \approx 1$ and higher powers of x are neglected.

$$K_p = \frac{64x^2}{27p^2} \quad \text{Since } K_p \text{ is constant at constant temperature } x \propto p.$$

or, *Yield of NH_3 is enhanced with the rise of pressure.*

Thus in the reaction where Δn is negative as in above (Here $\Delta n = 2-4 = -2$) the reaction is favoured at high pressure.

(2) $PCl_5 \leftrightharpoons PCl_3 + Cl_2$

Here products occupy larger volume than the reactant $\Delta n = 2-1 = 1$.

In the above dissociation of PCl_5 we have shown (previous section)

$$K_p = \frac{x^2 \cdot p}{a^2 - x^2}$$

K_p is constant at constant temperature. An increase of pressure would decrease x i.e., extent of dissociation. Thus if pressure is increased the yield of PCl_3 and Cl_2 will be poor i.e., dissociation of PCl_5 is diminished.

Thus in any gaseous reaction involving increase of volume (Δn is positive) i.e., where products occupy larger volume than the reactants, the reaction should be conducted at low pressure for favourable yield of the products.

(3) Let us now consider a third reaction of the type where no change of volume takes place ($\Delta n = 0$).

$$H_2 + I_2 \leftrightharpoons 2HI$$—

We recall in the previous section which indicates—

$$K_p = \frac{4x^2}{(a-x)(b-x)}$$

The term p does not appear either in numerator or in denominator of the equation. x is thus independent of p i.e., the yield of HI will not be influenced by the applied pressure at all. Thus, according to Le Chatelier *change of pressure would not affect a chemical equilibrium that involves a reversible reaction where $\Delta n = 0$* i.e., no volume change occurs.

It is important to keep in mind that change of pressure do not change the value of K so long as the temperature remains constant, rather it changes the concentration of the gaseous substances.

- **Effect of pressure on certain reversible reactions :**

Reaction	Increase of pressure	Decrease of pressure
$N_2 + O_2 \leftrightharpoons 2NO$	Since volume change is zero i.e., $\Delta n = 0$, increase of pressure will not effect the point of equilibrium.	Same as in increase of pressure.

Reaction	Increase of pressure	Decrease of pressure
$N_2 + 2H_2 \rightleftharpoons 2NH_3$	(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ In the forward reaction volume is decreased ($\Delta n = -2$). Increase of pressure will favour the yield of NH_3 (b) In the backward reaction $2NH_3 \rightarrow N_2 + 3H_2$, volume of the product is more than that of the reactant ($\Delta n = +2$). Hence this reaction will not be favoured and yield of N_2 and H_2 is less.	(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ Since volume in the forward reaction is less, decrease of pressure will not favour the forward reaction. Yield of NH_3 is less. (b) $2NH_3 \rightarrow N_2 + 3H_2$ volume is increased in the reverse reaction. Hence yield of product will be favoured. Large amount of N_2 and H_2 will be formed.
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	(a) In the forward reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ the volume is increased ($\Delta n = 1$) yield of the products will not be favoured. Smaller amount of PCl_3 and Cl_2 will be obtained. (b) $PCl_3 + Cl_2 \rightarrow PCl_5$. In the reverse reaction the volume is diminished. Increase of pressure will, therefore favour yield of PCl_5	(a) Volume is increased in the forward reaction. Hence decrease of pressure will favour the formation of PCl_3 and Cl_2. (b) Decrease of pressure will not favour the reaction $PCl_3 + Cl_2 \rightarrow PCl_5$ as volume is diminished. Thus yield of PCl_5 will be diminished.

(3) **Effects of active mass :** When any species of the reactants or the products is added to the equilibrium mixture, the system would change in such a way so as to diminish the concentrations of the substance added. This only occurs if the reaction is in the direction in which the added substance is used up in the reaction.

Whenever a component of the reactants is added, its concentration is enhanced. In order to neutralise it, some of the added component undergoes reaction to form the products increasing its concentration. The equilibrium is shifted towards right i.e., more products are formed because K_c remains constant at constant temperature. Again if some component of the products is removed from the vicinity of the equilibrium, the reaction proceeds towards right and as a result more products are formed. Similarly if some component of the products is added at equilibrium, the forward reaction is suppressed and the yield of the reactants is enhanced.

Let us consider the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_C = \frac{[NH_3]^2}{[N_2]\ [H_2]^3}$$

If we now add NH_3 from outside, the numerator increases so the denominator must increase to maintain K_C constant. The equilibrium is, therefore, displaced towards left—concentration of N_2 and H_2 is increased and backward reaction is favoured. Thus *the addition of any component of the reactants at equilibrium, displaces it in such a manner so as to consume that substance i.e., equilibrium is shifted from left to right. Conversely, removal of a substance will result in the reaction moving in the direction that forms more of that substance.*

Thus in the above equilibrium if the produced NH_3 is removed continuously from the reacting system, the equilibrium will be shifted towards right to form more ammonia. The yield of NH_3 in the Haber's process is increased to a large extent by liquefying NH_3, which is removed. However, it is to be noted that for a gaseous system the above statement is valid only if the volume of the system is kept unchanged. If the pressure remains constant but the volume is increased, the equilibrium will actually be shifted in the opposite direction. However this depends upon the value and sign of Δn (change of molecule) and the number of molecules of the substance added at equilibrium.

(4) Effect of volume change : If the volume of the vessel which contains the gas mixture in equilibrium is increased without changing the temperature, the pressure will decrease. According to Le Chateliers principle the equilibrium will be shifted in that direction where the pressure is increased i.e., the volume is more. Thus in the following reaction the equilibrium will shift to the left and the yield of NH_3 will be depressed if the reaction vessel is suddenly increased.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Change of volume does not affect the gaseous reaction which involves no change of volume ($\triangle n = 0$) e.g ;

$$N_2 + O_2 \rightleftharpoons 2NO$$

(5) Effect of adding Inert substance : If a non reacting substance be added to a system either at constant volume or at constant pressure, equilibrium may or may not be altered according to the condition of the reaction. Let us consider the thermal dissociation of PCl_5.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(i) *At constant pressure* if some nitrogen gas is introduced at equilibrium, the partial pressures of both reactants and products are decreased and the equilibrium is shifted in that direction where volume or number of molecules increases. Thus, in the above reaction, dissociation of PCl_5 will be favoured and more PCl_3 and Cl_2 will be formed.

In the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ if inert gas (Argon from air) is introduced keeping pressure constant, the partial pressures of N_2, H_2 and NH_3 will diminish although the total pressure remains constant and as such the reverse reaction will be favoured and as a result the yield of NH_3 is very much depressed.

(ii) *At constant volume* if some N_2 is introduced in the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ the total pressure of the mixture will increase but the partial pressure of the reactants and the products will not change. Hence point of equilibrium in this case will not be affected. Similarly if some inert gas be introduced in the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ total pressure will increase but the partial pressures of N_2, H_2 and NH_3 will remain unchanged since volume is not altered and so the equilibrium will be unaffected. *Thus it may be concluded that if an inert gas be introduced into a gaseous mixture at constant volume, the point of equilibrium will not be changed.*

- **Quantitative Fvaluation :—**

Let us consider the following reversible reaction $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$

We know, $K_p = K_x P^{\triangle n}$ $\qquad \triangle n = (\gamma + \delta) - (\alpha + \beta)$

$$K_p = \frac{X_C{}^{\gamma}\, X_D{}^{\delta}}{X_A{}^{\alpha}\, X_B{}^{\beta}}\, P^{\triangle n} \quad \ldots\ldots (1)$$

Let n_1, n_2, n_3, n_4 and n_0 be the number of moles of A, B, C, D and the added inert gas respectively.
Total number of moles at equilibrium $= n_1 + n_2 + n_3 + n_4 + n_0 = \Sigma N$
On adding inert gas, the value of ΣN increases.

$$X_A = \frac{n_1}{\Sigma N}, X_B = \frac{n_2}{\Sigma N}, X_C = \frac{n_3}{\Sigma N}, X_D = \frac{n_4}{\Sigma N}$$

So putting the value of X_A, X_B, X_C and X_D in equation (1),

$$K_P = \frac{\left(\frac{n_3}{\Sigma N}\right)^{\gamma} \left(\frac{n_4}{\Sigma N}\right)^{\delta}}{\left(\frac{n_1}{\Sigma N}\right)^{\alpha} \left(\frac{n_2}{\Sigma N}\right)^{\beta}} P^{\triangle n}$$

$$K_p = \frac{n_3{}^{\gamma}\, n_4{}^{\delta}}{n_1{}^{\alpha}\, n_2{}^{\beta}} \left(\frac{P}{\Sigma N}\right)^{\triangle n} \quad \ldots\ldots\ldots (2)$$

K_P is constant at constant temperature. The number of moles of the products or reactants depends upon the second factor $\left(\frac{P}{\Sigma N}\right)^{\Delta n}$ of the equation (2). Let us consider the effect of addition of inert gas at constant pressure and constant volume.

(A) Addition of Inert gas at constant pressure :

(i) **When $\Delta n=0$,** the second factor $\left(\frac{P}{\Sigma N}\right)^{\Delta n}=1$, and hence the first factor $\frac{(n_3)^{\gamma}(n_4)^{\delta}}{(n_1)^{\alpha}(n_2)^{\beta}}$ in equation (2) will not change and the equilibrium will not be disturbed. Hence in a reversible reaction where no change of number of mole or volume occurs as in $H_2 + I_2 \rightleftharpoons 2HI$, the point of equilibrium will not be altered if inert gas is added to it at constant pressure.

(ii) **If Δn is positive** then $\left(\frac{P}{\Sigma N}\right)^{\Delta n}$ decreases and hence first factor $\frac{(n_3)^{\gamma}(n_4)^{\delta}}{(n_1)^{\alpha}(n_2)^{\beta}}$ will increse in magnitude. The yield of the products increases and that of the reactants decreases ; equilibrium is shifted towards right.

Thus if we add some nitrogen gas at constant pressure in the following reaction at equilibrium, the concentration of Cl_2 and PCl_3 will increase. Here $\Delta n = +1$.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(iii) **If Δn is negative,** the second factor $\left(\frac{P}{\Sigma N}\right)^{\Delta n}$ increases so that the first factor $\frac{(n_3)^{\gamma}(n_4)^{\delta}}{(n_1)^{\alpha}(n_2)^{\beta}}$ in equation (2) is decreased. The concentration of the product decreases and that of the reactants increases. The point of equilibrium is shifted from right to left. Thus in the following reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta n = -2$$

If some argon gas is introduced at constant pressure, the equilibrium is shifted towards left, yield of NH_3 is decreased.

(B) Addition of Inert gas at constant volume :

When the inert gas is added to the system at constant volume an increase of ΣN will result in an exactly proportional increase of P, the ratio $P/\Sigma N$ remains unchanged. As a result of this the first factor of equation (2) remains constant and the equilibrium will not be disturbed.

Hence it may be said when inert gas is added to a system whose volume is kept constant, the point of equilibrium will remain unchanged irrespective of whether $\Delta n = 0$, positive or negative.

(5) Influence of catalyst :

According to Le Chatelier's principle presence of a catalyst is not given any importance at all in a reversible reaction since the point of equilibrium is not changed by the use of catalyst. A catalyst cannot alter the composition of the equilibrium mixture in a reversible reaction. It speeds up both the forward and backward reaction

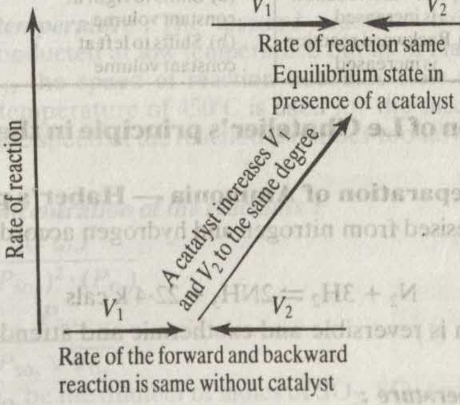

V_1
V_2
Rate of reaction same
Equilibrium state in
presence of a catalyst
Rate of reaction
A catalyst increases V_1
and V_2 to the same degree
V_1
V_2
Rate of the forward and backward
reaction is same without catalyst

Fig 10.5. : Equilibrium in presence of a catalyst.

to the same extent. Equilibrium is attained more rapidly but the value of K remains unchanged. However, a catalyst alters the rate of a chemical reaction and therefore alters the velocity constant of the reaction but since the rate constants for the forward and backward reaction are changed to exactly the same degree, their ratio remains constant. Thus a catalyst may alter the rate of approach to equilibrium which may be attained quickly but the value of K is not changed at all.

Summary : The following table summarises the effects of temperature, pressure, inert gas and catalyst on rate, composition of equilibrium mixture and equilibrium constant of a reversible reaction.

Reaction parameters	Rate of reaction	Composition of equilibrium mixture	Equilibrium constant (K)
1. (a) Increase of pressure. (b) Decrease of pressure.	(a) Increases for gaseous reaction (b) Decreases for gaseous reaction	(a) Changes in Δn—may be positive or negative (b) Same as above	(a) Unchanged (b) Unchanged
2. Use of catalyst	Changes	No change	No change
3. (a) Increase of tempurature (b) Decrease of temperature	(a) Increases (b) Decreases	(a) Changes (b) Changes	(a) Changes (b) Changes $\frac{d \ln K_p}{dt} = \frac{\Delta H}{RT^2}$
4. Inert gas	No change	At constant volume no change. At constant pressure if $\Delta n = 0$, no change. If Δn is negative the yield of the product is depressed. If Δn is positive the. yield is increased.	No change
5. (a) Addition of reactant. (b) Addition of products.	(a) Forward reaction is increased (b) Backward reaction is increased	(a) Shifts to right at constant volume (b) Shifts to left at constant volume	No change No change

10.14. Application of Le Chatelier's principle in the manufacturing process.

(1) Industrial preparation of Ammonia — Haber's process :

Ammonia is synthesised from nitrogen and hydrogen according to the following equation.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22{\cdot}4 \text{ k cals}$$

The above reaction is reversible and exothermic and attended with decrease in volume.

[A] ***Effects of temperature :***

Since the forward reaction is exothermic if heat is applied to the system the point of equilibrium will be shifted in that direction where the heat is consumed. Since backward reaction is endothermic the reaction will proceed in the reverse direction and yield of NH_3 is depressed. Hence the reaction should be conducted at low temperature, but at low temperature the speed of the reaction is too slow. Hence an optimum temperature is worked out where the speed of the reaction is neither too slow nor the yield of NH_3 is low. The *optimun temperature* in Haber's process is 550°C. Every exothermic reaction is characterised by an optimum temperature.

[B] ***Effect of pressure :***

$$\underset{1\text{vol}}{N_2} + \underset{3\text{ vol}}{3H_2} \rightleftharpoons \underset{2\text{ vol}}{2NH_3}$$

According to Le Chatelier's principle, in a reversible reaction where products occupy smaller volume than the reactants, the high pressure favours the forward reaction. A pressure as high as 200 atmosphere is applied in Haber's process to get a better yield.

[C] ***Effects of catalyst :***

We know a catalyst cannot alter the point of equilibrium in a reversible reaction. Catalyst only helps to attain the equilibrium quickly by increasing the rate of the reaction. The catalyst used in Haber's process is *finely powdered iron with molybdenum as promoter*. The rate of reaction increases at 550°C and the production time becomes quick.

[D] ***Effect of concentration :***

According to Le Chatelier's principle if the concentration of NH_3 is diminished, the point of equilibrium is shifted towards right. Hence NH_3 is removed as soon as it is formed from the vicinity of the products by liquefying it immediately. As a result yield of NH_3 is enhanced.

(2) Manufacture of SO_3 by contact process :

The oxidation of SO_2 by air to produce SO_3 is commercially employed in the manufacture of sulphuric acid by contact process.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45 \text{ k cal}$$

The above reaction is reversible, exothermic and attended with decrease of volume.

(a) ***Influence of temperature :*** The forward reaction being exothermic, the reaction should be conducted at low temperature but as in Haber's process for the manufacture of NH_3, the speed of reaction becomes slow at low temperature. Hence an optimum temperature of 450°C is used for the successful conversion of SO_3 from SO_2 when the speed of the reaction is neither too slow nor the yield of SO_3 is low.

(b) ***Influence of concentration of the reactants :***

$$K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 \cdot (P_{O_2})}$$

$$\text{or} \quad K_p = \frac{P_{SO_3}}{P_{SO_2}\sqrt{P_{O_2}}} \quad \text{..............................} \quad (1)$$

Let n_{SO_3}, n_{SO_2} and n_{O_2} be the number of moles of SO_3, SO_2 and O_2 respectively. Let N be the total number of moles at equilibrium, p be the total pressure.

$$P_{SO_3} = \frac{n_{SO_3}}{N} \cdot p \qquad P_{SO_2} = \frac{n_{SO_2}}{N} \cdot p \qquad P_{O_2} = \frac{n_{O_2}}{N} \cdot p$$

Substituting these in equation (1),

$$K_p = \frac{\frac{n_{SO_3}}{N}\cdot p}{\frac{n_{SO_2}}{N}\cdot p\sqrt{\frac{n_{O_2}}{N}\cdot p}}$$

$$K_p = \frac{n_{SO_3}}{N}\cdot p\times \frac{N}{n_{SO_2}}\cdot\frac{1}{p}\times\sqrt{\frac{N}{n_{O_2}\cdot p}}$$

$$= \frac{n_{SO_3}}{n_{SO_2}}\cdot\sqrt{N}\cdot\frac{1}{\sqrt{n_{O_2}\times p}}$$

$$\text{or,}\quad \frac{n_{SO_3}}{n_{SO_2}} = K_p\cdot\sqrt{p}\cdot\sqrt{\frac{n_{O_2}}{N}} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

It is evident from equation (2) that number of moles of SO_3 will be influenced by number of moles of O_2. Hence if pure oxygen is used for oxidation then yield of SO_3 will be very much increased but in practice air is used for the oxidation of SO_2. Air contains about 78% by volume of nitrogen. If excess of air is used for the oxidation of SO_2 then N also increases which in turn, decreases the yield of SO_3 $\left[n_{SO_3} \propto \frac{1}{\sqrt{N}}\right]$.

Thus only a moderate excess of air is used in practice for the oxidation of SO_2.

(c) ***Influence of pressure :*** It is expected from Le Chatelier's principle that since the volume is diminished in the forward reaction, the reaction should be conducted at high pressure in order to have favourable yield of SO_3. But a close scrutiny of equation (2) shows that at *equilibrium* $\frac{n_{SO_3}}{n_{SO_2}} \propto \sqrt{p}$ if $\frac{n_{O_2}}{N}$ is constant. Hence increase of pressure will increase the yield of SO_3 but the effect is so relatively small that little or no advantage is taken of it in industrial practice if an effective catalyst is employed. The pressure employed in contact process using platinised asbestos is 1 to 1·5 atmosphere.

(d) ***Catalyst :*** Different contact catalysts are used in different plants. In **Bedische process** the catalyst is platinised asbestos. Burnt pyrites consisting of Fe_2O_3 and CuO is used as a contact catalyst in **Mannheim process.** The most popular catalyst is V_2O_5 prepared by igniting zeolite impregnated with V_2O_5. Unlike Pt. asbestos catalyst, it is not so easily poisoned.

(3) Industrial preparation of Nitric acid—Birkland and Eyde process.

Here the raw materials are aerial Nitrogen and Oxygen which unite to form Nitric oxide according to the following equation.

$$N_2 + O_2 \rightleftharpoons 2NO - 21{\cdot}6 \text{ k cal/mole.}$$

The reaction is reversible, endothermic and does not involve any change of volume ($\triangle n = 0$).

(a) ***Influence of temperature :*** Since the reaction is endothermic, the yield of NO is favoured at high temperature. In practice a temperature as high as 3000°C is used through electric spark.

(b) ***Influence of pressure :*** Since the above equation does not involve any change of volume i.e., $\triangle n = 0$. Pressure will not have any effect on equilibrium according to Le Chatelier's principle.

(c) ***Effect of concentration :*** Increase of concentration of N_2 and O_2 and decrease of concentration of NO will increase the yield of NO. Hence in this reaction large excess of N_2 and O_2 is used and the NO thus produced is immediately removed from the reactor in order to decrease the rate of reverse reaction and consequently the yield of NO is enhanced.

The overall equations leading of HNO_3 manufacture by Birkland-Eyde process is as follows :—

$$\begin{array}{lclcll}
N_2 & + & O_2 & \overset{3000^\circ C}{\rightleftharpoons} & 2NO & -21{\cdot}6\text{ k cal/mole} \\
2NO & + & O_2 & \rightleftharpoons & 2NO_2 & \\
2NO_2 & + & H_2O & = & HNO_2 & +HNO_3 \\
3HNO_2 & = & HNO_3 & + & 2NO & +H_2O
\end{array}$$

The following table summarises the optimum conditions, according to Le Chatelier's Principle, for the manufacture of certain important compounds.

Products	Equation	Conditions for maximum yield of the products			
		Temperature	Pressure	Concentration	Catalyst
1. Haber's process—Manufacture of Ammonia	$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)+22{\cdot}4$ kcal (i) Reversible (ii) Exothermic (iii) Decrease of volume, hence decrease of pressure	Low temperature. Optimum temperature = 550°C	High pressure =200 atmospheric pressure	High concentration of N_2 and H_2 and NH_3 is removed as soon as it is formed.	Iron powder + Molybdenum as promoter
2. Manufacture of Sulphuric acid by contact process	$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)+45$ kcals/mole Same as above	Low temperature, Optimum temperature = 450°C	High Pressure. In practice high pressure not required.	Moderate excess of air and simultaneous removal of SO_3	Pt. asbestos or V_2O_5
3. Manufacture of Nitric acid by Birkland Eyde process	$N_2(g)+O_2(g) \rightleftharpoons 2NO(s) -21{\cdot}6$ kcal/mole (1) Reversible (2) Endothermic, (3) No change of volume and hence no change of pressure	High temperature 3000°C	No influence of pressure	Excess of N_2 and O_2 and removal of NO	——
4. Manufacture of Hydrogen by Bosch process	$CO+H_2O \rightleftharpoons CO_2 +H_2+Q$ cals (1) Reversible (2) Exothermic (3) No change of volume or pressure	Low temperature. Optimum temperature = 400°C	No influence of pressure	Excess steam	Fe_2O_3

10.15. Le Chatelier's principle in physical equilibrium.

Like chemical equilibrium Le Chatelier's principle is also applicable in certain physical equilibrium, some of them are discussed here in a nut shell.

(1) Ice-water equilibrium (melting of ice) :

$$\underset{\text{Large vol}}{\boxed{\text{Ice}}} \rightleftharpoons \underset{\text{Small vol}}{\boxed{\text{Water}}} - \boxed{\text{Heat}}$$

The above physical change of conversion of ice into water is (i) reversible, (ii) endothermic and (iii) volume is decreased. Therefore, applying Le Chatelier's principle,

(i) When pressure is increased the point of equilibrium will be shifted in that direction where decrease of volume takes place i.e., ice is converted into water. Decrease of pressure will favour reverse reaction.

(ii) Since the forward reaction is endothermic, the increase of temperature favours the conversion of ice into water. Phase rule study of ice-water-water vapour system shows that melting point of ice decreases with the increase of pressure. According to Le Chatelier's principle this decrease of melting point with the increase of pressure is related to increase in volume or decrease in density on solidification. Thus on increasing pressure, ice will melt since applied pressure will be relieved on melting as volume is decreased. Ice-skating and flow of glaciers are based upon this consideration.

(2) Water-steam equilibrium (Boiling of water) :

$$\underset{\text{Less vol}}{\boxed{\text{Water}}} \rightleftharpoons \underset{\text{Large vol}}{\boxed{\text{Steam}}} - \boxed{\text{Heat}}$$

The above physical process is (i) reversible, (ii) endothermic and (iii) volume of the product is increased. Hence according to Le Chatelier's principle,

(i) Increase of pressure causes backward reaction as in the backward reaction the volume is diminished. Steam will be condensed into water on applying pressure upon it. Decrease of pressure helps in the evaporation of water into steam.

(ii) Increase of temperature causes the equilibrium to shift towards right and as a result more water will be converted into steam. Decrease of temperature on the otherhand helps in the condensation of steam into water.

(3) Solubility of substances :

(i) For most of the gases it is observed that when those are dissolved in water, heat is evolved. Hence on the basis of Le Chatelier's principle it is expected that solubility of gas will decrease when temperature is increased. Hydrogen and inert gases, however, behave differently over some ranges of temperature. Similarly increase of pressure increases the solubility of gas in water.

(ii) In a saturated solution let us assume that some undissolved solid solute is in equilibrium with that in solution.

(a) Now if the process of dissolution be an endothermic one then increase of temperature will increase its solubility.

$$\underset{\text{solid}}{NH_4Cl} + \text{water} \rightleftharpoons \underset{\text{soluble}}{[NH_4^+ + Cl^-]} - [\text{Heat}]$$

It is for this reason, as a consequence of Le Chatelier's principle that solubilities of most of the solids increase with the increase of temperature. Examples are KCl, KNO_3, $NaNO_3$ etc.

(b) If, however, during dissolution of a solid in water heat is evolved, its solubility in water decreases with the increase of temperature which is in accordance with Le Chaterlier's principle.

$$\underset{\text{solid}}{NaOH} + \text{water} \rightleftharpoons \underset{\text{soluble}}{[Na^+ + OH^-]} + [\text{Heat}]$$

Examples being sodium carbonate monohydrate, anhydrous sodium sulphate, calcium acetate etc.

Thus solubility of NaOH in cold water is more than in hot water.

10.16. All reactions are reversible.

Every reaction has its own velocity. Some reactions are very fast, some are exceedingly slow. In some reactions, the reactant particles react very quickly to form the products but the latter are not able to react in the same rate as the former e.g.,

$$2KClO_3 = 2KCl + 3O_2$$

But close examinations of reactions shows that all reactions are reversible. But all of which we are, unfortunately, unable to study with technique at our disposal. The forward reaction is so fast and the corresponding backward reaction is so slow that we assume the reaction to be irreversible. But if the same reaction is carried out in closed vessel to prevent escape of reactants and products, the physical conditions are changed or the concentrations of the reactants and products are altered, the apparently irreversible reaction may be made reversible provided the reaction is not too fast and possesses measurable rate. But their are some special reactions which becomes irreversible due to certain reasons.

(i) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

If the raction is carried out in open vessel, hydrogen gas escapes from the medium. Therefore, the molar concentration or partial pressure of hydrogen is assumed to be zero.

$$K_C = \frac{[ZnSO_4] \times [H_2]}{[Zn]\,[H_2SO_4]}$$

Since K_C is constant at a constant temperature and $P_{H_2} = 0$, large quantity of Zn and H_2SO_4 react to proceed in the forward direction and the reaction becomes irreversible.

(ii) $NaOH + HCl \rightarrow NaCl + H_2O$

Strong acid HCl react with strong base NaOH to produce salt NaCl and water. The medium contains H^+, Cl^-, Na^+ and OH^+ ions. H^+ ion of acid reacts with OH^- ion of alkali to form practically undissociated weak electrolyte H_2O molecule and thus H^+ and OH^- ions are constantly removed from the sphere of action. The concentration of H^+ and OH^- ions produced from the dissociation of H_2O are so small as to be neglected. Consequently the H^+ and OH^- ions combine to from H_2O and thus the reaction proceeds in one direction and the overall reaction goes to completion.

(iii) $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

The aqueous solution contains Ag^+, NO_3^-, Na^+ and Cl^- ions. Ag^+ ion combines with Cl^- ion to form insoluble white ppt of AgCl and are removed from the medium. Thus the concentration of Ag^+ and Cl^- appreciably decreases. To maintain K_C constant, more $AgNO_3$ reacts with NaCl to make the reaction complete. *Thus all precipitation reactions are complete and irreversible.*

(iv) $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2\uparrow + H_2O$

In the above reaction, as soon as CO_2 is formed it escapes from the medium. The partial pressure of CO_2 thus becomes 0. Forward reaction must continue to make K_C constant till the reaction is complete.

10.17. Some special problems solved.

1. *What will happen if pressure is increased or excess CO is added in the following reaction ?*

$$NO_2 + CO \rightleftharpoons NO + CO_2$$

Ans : The above is an example of homogeneous reversible gaseous reaction. The total number of moles before and after the reaction is 2. ($\Delta n = 0$). According to Le Chatelier's principle since there is no change of volume, increase or decrease of pressure will not have any effect on the point of equilibrium. This can be shown as follows :—

	NO_2 +	CO ⇌	NO +	CO_2
Initially	1 mole	1 mole	0 mole	0 mole
Number of moles at equilibrium	$(1-x)$	$(1-x)$	x	x

Let x moles of NO_2 disappear at equilibrium and at equilibrium the volume be V litre.

$$[NO_2] = \frac{1-x}{V}\ ; [CO] = \frac{1-x}{V}\ ; [NO] = \frac{x}{V}\ ; [CO_2] = \frac{x}{V}$$

We know, $PV = nRT$ or, $P = CRT$

Let $P_{NO_2}, P_{NO}, P_{CO_2}, P_{CO}$ be their partial pressures.

$$P_{NO_2} = [NO_2]RT = \frac{1-x}{V}RT$$

$$P_{NO} = [NO]RT = \frac{x}{V}RT$$

$$P_{CO} = [CO]RT = \frac{1-x}{V}RT$$

$$P_{CO_2} = [CO_2]RT = \frac{x}{V}RT$$

$$\text{Now, } K_P = \frac{P_{NO} \times P_{CO_2}}{P_{NO_2} \times P_{CO}} = \frac{\frac{x}{V}RT \times \frac{x}{V}RT}{\frac{1-x}{V}RT \times \frac{1-x}{V}RT}$$

$$\text{or, } K_P = \frac{x^2}{(1-x)^2}$$

The above equation does not contain the term P or V. *Hence the reaction is independent of pressure.*

If CO is added from outside, at equilibrium, the concentration of CO is increased. Since K_P is constant at constant temperature, more CO will react with NO_2 to neutralise the excess partial pressure of CO, as a result the rate of forward reaction will increase and yield of NO and CO_2 will hence increase.

2. $P + 3Q \rightleftharpoons 2M + N + k\ cals$

How would the equilibrium be effected in the above reaction if (i) temperature is increased, (ii) concentration of Q is increased, (iii) pressure is increased.

Ans : (i) The forward reaction is exothermic. Hence increase of temperature favours the point of equilibrium towards that direction where heat is consumed, that is left hand direction. The yield of M and N would decrease at high temperature or M and N will combine to form P and Q or in other words forward reaction is depressed.

(ii) To maintain K_C constant the yield of M and N would increase when the concentration of Q is increased at equilibrium.

(iii)
$$\begin{array}{ccccccc} P & + & 3Q & \rightleftharpoons & 2M & + & N \\ \text{1 vol} & & \text{3 vol} & & \text{2 vol} & & \text{1 vol} \\ & \text{Total = 4 vol} & & & & \text{Total = 3 vol} & \end{array}$$

The reaction is attended with decrease of volume ($\triangle n = -1$). According to Le Chatelier's principle in a reversible gaseous reaction where products occupy smaller volume than the reactants, the forward reaction is favoured at high pressure. Hence if pressure is increased the yield of M and N is enhanced.

3. $2CO + O_2 \rightleftharpoons 2CO_2 + Q$ *cals.*

The reaction is not complete. State conditions how to make the above reaction complete.

Ans : (a) The forward reaction is exothermic. According to the Le Chatelier's principle if heat is applied, yield of the product will decrease and that of reactants will increase. Decrease of temperature will favour the yield of CO_2.

(b) Here $\triangle n = -1$ i.e., volume is decreased. Hence increase of pressure will favour the yield of CO_2.

(c) If excess O_2 is introduced at equilibrium, the rate of forward reaction increases to make K_p constant as the partial pressure of O_2 is increased. As a result the yield of CO_2 is enhanced.

(d) On removing CO_2 as soon as it is formed from equilibrium mixture, the concentration of CO_2 would decrease. CO and O_2 would further react to make K_P constant and increase the concentration of CO_2. Yield of CO_2 is favoured.

Thus for favourable yield of CO_2 i.e., to make the reaction as complete as possible, the following 4 conditions are to be maintained.

(i) Low temperature, (ii) High pressure, (iii) Increasing concentration of O_2 i.e., use of excess O_2 and (iv) Removal of CO_2 as soon as it is formed.

4. *State five conditions by which the point of equilibrium of the following reversible reaction can be shifted towards left.*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + Q \text{ cals}$$

Ans : (a) Decreasing the concentration of nitrogen.
(b) Decreasing the concentration of hydrogen.
(c) Increasing the concentration of ammonia.
(d) Increasing the temperature.
(e) Decreasing the pressure.

5. *For the reaction* $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$ *the forward reaction at constant temperature is favoured by*

(a) Introducing an inert gas at constant volume.
(b) Introducing chlorine gas at constant volume.
(c) Introducing an inert gas at constant pressure.
(d) Increasing the volume of the container.
(e) Introducing PCl_5 *at constant volume.* [*I.I.T. 1991*]

Ans : (c) (d) (e)

6. *An example of a reversible reaction is*

(a) $Pb(NO_3)_{2(aq)} + 2NaI_{(aq)} \rightarrow PbI_{2(s)} + 2NaNO_{3(aq)}$
(b) $AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$
(c) $2Na_{(s)} + H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$
(d) $KNO_{3(aq)} + NaCl_{(aq)} \rightarrow KCl_{(aq)} + NaNO_{3(aq)}$

[*I.I.T. 1985*]

Ans : (d)

7. *Powdered* $CaCO_3$ *is heated in open air. Explain whether equilibrium would be attained or not.* [*W.B.J.E.E. 1889*]

Ans : $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

The reaction is reversible. Since on heating CO_2 escapes from the medium, the reverse reaction does not occur, only forward reaction proceeds till the reaction is complete, equilibrium as a result is never reached.

However, if the reaction is allowed to take place in a closed vessel, equilibrium is reached. On heating in a closed vessel, the concentrations of CaO and CO_2 are increased when they start reacting to form $CaCO_3$. When the rate of forward and backward reaction becomes equal, equilibrium is reached.

8. $4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g) + 27$ k cals.

Explain how the concentration of chlorine would change at equilibrium with the change of following conditions.

(a) Increase of the concentration of O_2, (b) Decrease of total pressure, (c) Increase of temperature, (d) Addition of catalyst, (e) Volume of the container is increased.

Ans : (a) When the concentration of O_2 is increased, the equilibrium will be shifted in that direction where the concentration of O_2 is decreased. Thus to maintain K_p constant, the forward reaction is favoured. As a result, concentration of Cl_2 will increase and that of O_2 will decrease.

(b) $\Delta n = -1$, the products occupy smaller volume than the reactants. The forward reaction is favoured at high pressure. Therefore, when pressure is decreased, the reverse reaction is favoured and the concentration of Cl_2 would diminish.

(c) The forward reaction is exothermic. Hence the increase of temperature, following Le Chatelier's principle will shift the equilibrium in the direction which absorbs heat and decrease of temperature will shift the equilibrium in the direction which evolves heat. Thus in the above reaction when temperature is increased equilibrium will be shifted from right to left. Hence the concentration of chlorine will diminish.

(d) Since catalyst has no effect on equilibrium, it will not be able to change the concentration of Cl_2.

(e) If the volume of the container is increased, the total pressure would decrease. Decrease of pressure will shift the equilibrium in that direction where the volume or number of moles increases. Here $\Delta n = -1$. Number of moles in the L.H.S. is more than that in R.H.S. Therefore, equilibrium will be shifted towards left on increase of volume. As a consequence of this the concentration of Cl_2 would diminish.

9. *If x be the mole fraction of NH_3 at equilibrium and p be total pressure, find an equation connecting p, x and the equilibrium constant K_p for the following reaction.*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

[W.B.J.E.E. 1986]

Also show that x increases with p.

Ans : At the start molar ratio of $N_2 : H_2 = 1 : 3$. Since x is the mole fraction of NH_3 at equilibrium, the mole fraction of the reactants together is $1-x$. Since N_2 and H_2 react in the ratio of $1 : 3$, their mole fraction at equilibrium will also be in that ratio.

	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
Mole fraction at equilibrium	$\frac{1}{4}(1-x)$		$\frac{3}{4}(1-x)$		x

$p_{N_2} =$ partial pressure of $N_2 = \dfrac{1-x}{4}.p$

$p_{H_2} =$ " " " $H_2 = \dfrac{3}{4}(1-x).p$

$p_{NH_3} =$ " " " $NH_3 = x.p$

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} \quad \text{or, } K_p = \frac{(xp)^2}{\left[\frac{1-x}{4}\cdot p\right]\left[\frac{3}{4}(1-x).p\right]^3}$$

$$\text{or, } K_p = \frac{x^2p^2}{\left[\frac{1-x}{4}\cdot p\right]\left[\frac{27}{64}(1-x)^3.p^3\right]} \quad \text{or, } K_p = \frac{256x^2}{27(1-x)^4p^2}$$

Since x is small, $1-x \approx 1$

$K_p = \frac{256x^2}{27p^2}$ This is the relation among x, p and K_p

Since K_p, 256 and 27 are constants $x^2 \propto p^2$ or $x \propto p$

If the pressure is increased the mole fraction of NH_3 will also increase.

10.18. Numerical Examples.

1. *At 30 atmospheric pressure and 350°C, the molar ratio of N_2 and H_2 in a mixture is 1 : 3. The percentage of NH_3 at equilibrium is 17%. Calculate the equilibrium constant of the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$.*

Ans : The partial pressure of a constituent in a mixture is proportional to its percentage. Again partial pressure = Mole fraction × Total pressure.

$$\text{Again, mole fraction} = \frac{\text{percentage}}{100}$$

$$\therefore P_{NH_3} = \frac{17}{100} \times 30 = 5.1 \text{ atmosphere}$$

$$\therefore (P_{N_2} + P_{H_2}) = \left(1 - \frac{17}{100}\right) \times 30 \text{ atmosphere} = (1 - 0{\cdot}17) \times 30 \text{ atmosphere}$$

Ratio of the two gases = 1 : 3

$$P_{N_2} = \frac{1}{4}(1 - 0{\cdot}17) \times 30 = 6.225 \text{ atmosphere}$$

$$P_{H_2} = \frac{3}{4}(1 - 0{\cdot}17) \times 30 = 18{\cdot}675 \text{ atmosphere}$$

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3} \quad K_p = \frac{(5{\cdot}1)^2}{6{\cdot}225 \times (18{\cdot}675)^3} = 6{\cdot}4 \times 10^{-4} \quad K_p = 6{\cdot}4 \times 10^{-4}$$

2. *2 moles of PCl_5 were heated in a closed flask of two litre capacity. At equilibrium PCl_5 is dissociated to the extent of 40%. Calculate equilibrium constant of the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.*

Ans : 40% of 2 mole PCl_5 $= \frac{40 \times 2}{100} = 0{\cdot}8$ mole

$[PCl_5]$ at equilibrium $= \frac{2 - 0{\cdot}8}{2} = 0{\cdot}6$ mole

$[PCl_3]$ " " $= \frac{0{\cdot}8}{2} = 0{\cdot}4$ mole

$[Cl]$ " " $= \frac{0{\cdot}8}{2} = 0{\cdot}4$ mole

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0{\cdot}4 \times 0{\cdot}4}{0{\cdot}6} = 0{\cdot}267$$

$$K_c = 2{\cdot}67 \times 10^{-1}$$

3. *Bodenstein mixed 8·07 ml of hydrogen at N.T.P. with 0·1052 g of iodine in a sealed tube and heated the tube at 448°C for some time. The tube when suddenly cooled and broken gave 0·0763 g of HI. Calculate the equilibrium constant of the reaction. $H_2 + I_2 \rightleftharpoons 2HI$.*

Ans : $$8{\cdot}07 \text{ ml of } H_2 = \frac{8{\cdot}07}{22400} = 3{\cdot}60 \times 10^{-4} \text{ mole of } H_2$$

$$0{\cdot}1052 \text{ g of } I_2 = \frac{0{\cdot}1052}{254} = 4{\cdot}14 \times 10^{-4} \text{ mole of Iodine}$$

$$0{\cdot}0763 \text{ g of HI} = \frac{0{\cdot}0763}{128} = 5{\cdot}96 \times 10^{-4} \text{ mole of HI.}$$

As already mentioned earlier (see 10.13), k for the reaction $H_2 + I_2 \rightleftharpoons 2HI$.

$K = \dfrac{4x^2}{(a-x)(b-x)}$ where a mole of H_2 react with b mole of I_2 to form $2x$ moles of HI.

$$K = \frac{(5{\cdot}96 \times 10^{-4})^2}{(3{\cdot}60\times10^{-4} - 2{\cdot}98\times10^{-4})\,(4{\cdot}14\times10^{-4} - 2{\cdot}98\times10^{-4})}$$

$$k = \frac{(5{\cdot}96)^2}{0{\cdot}62 \times 1{\cdot}16} = 49{\cdot}40$$

4. *At 250°C, 1 litre of partially dissociated PCl_5 gas at 1 atmosphere, weighs 2·690 g. Calculate the degree of dissociation (α) and calculate the equilibrium constant K_p.*

Ans : If 1 mole of a gas yields γ moles of gaseous products

$$\alpha = \frac{M_1 - M_2}{M_2(\gamma - 1)}$$

Where M_1 is the molecular weight of the undissociated gas and M_2 is the average molecular weight of the gases when the gas is partially dissociated.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Here M_1 = Molecular weight of $PCl_5 = 208{\cdot}3, \quad \gamma = 2\ ; \quad \alpha = \dfrac{M_1 - M_2}{M_2}$

$$M_2 = \frac{w.RT}{P.V} = \frac{(2{\cdot}690\text{ g})\,(0{\cdot}082 \text{ lit atmos deg}^{-1}\text{ mole}^{-1})\,(523\text{ K})}{1 \text{ atmos} \times 1 \text{ lit.}} = 115{\cdot}36 \text{ g mole}^{-1}$$

$$\alpha = \frac{208{\cdot}3 - 115{\cdot}36}{115{\cdot}36} = 0{\cdot}8$$

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Number of moles at the start	1		0		0
All equilibrium numbers of mole	$1-\alpha$		α		α

Total number of moles at equilibrium $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$P_{PCl_5} = \frac{1-\alpha}{1+\alpha}.p \qquad P_{PCl_3} = \frac{\alpha}{1+\alpha}.p \qquad P_{Cl_2} = \frac{\alpha}{1+\alpha}.p$$

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\left(\dfrac{\alpha}{1+\alpha}\ p\right)\left(\dfrac{\alpha}{1+\alpha}\ .p\right)}{\left(\dfrac{1-\alpha}{1+\alpha}\right).P}$$

$$K_p = \frac{\alpha^2 p}{1-\alpha^2} = \frac{(0{\cdot}8)^2 \times 1}{1-(0{\cdot}8)^2} = 1{\cdot}78 \quad \text{or, } K_p = 1{\cdot}78$$

5. *How many moles of PCl_5 must be added to a litre vessel at 250°C in order to obtain a concentration of 0·1 mole of chlorine per litre.* (*Given $K_p = 1{\cdot}78$*).

Ans : Let x be the number of moles of PCl_5 added to the vessel.

$$K_p = 1{\cdot}78 = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\left[0{\cdot}1\ \dfrac{RT}{V}\right]\left[0{\cdot}1\ \dfrac{RT}{V}\right]}{(x - 0{\cdot}1)\ \dfrac{RT}{V}} = \frac{(0{\cdot}1)^2}{x - 0{\cdot}1}\ \frac{RT}{V}$$

$$\text{or, } 1{\cdot}78 = \frac{0{\cdot}01}{x - 0{\cdot}1} \cdot \frac{0{\cdot}082 \times 523}{1} \qquad \text{or, } x = 0{\cdot}341 \text{ mole}$$

Number of moles of PCl_5 added $= 0{\cdot}341$

6. *One mole of acetic acid is mixed with 1 mole of ethanol at 25°C and after equilibrium is reached a titration with standard alkali solution shows that 0·667 moles of acetic acid has reacted.*

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Calculate equilibrium constant (K_x) in term of moles fraction. When 0·500 mole of ethanol is added to 1·00 mole of acetic acid at 25°C how much ester (x) will be formed and how much acetic acid will remain unreacted at equilibrium ?

Ans : $X_{CH_3COOH} = \dfrac{1{\cdot}000 - 0{\cdot}667}{2}, \quad X_{C_2H_5OH} = \dfrac{1{\cdot}000 - 0{\cdot}667}{2}$

$X_{CH_3COOC_2H_5} = \dfrac{0{\cdot}667}{2}, \qquad X_{H_2O} = \dfrac{0{\cdot}667}{2}$

Where x denotes mole fraction of the species

$$K_x = \frac{X_{CH_3COOC_2H_5}\, X_{H_2O}}{X_{CH_3COOH}\, X_{C_2H_5OH}}$$

$$= \frac{\dfrac{0{\cdot}667}{2} \times \dfrac{0{\cdot}667}{2}}{\left(\dfrac{1{\cdot}000 - 0{\cdot}667}{2}\right)\left(\dfrac{1{\cdot}000 - 0{\cdot}667}{2}\right)} = 4$$

$K_x = 4$

Now $K_x = 4 = \dfrac{x \times x}{(1{\cdot}000 - x)(0{\cdot}500 - x)}$

or, $x = 1{\cdot}577$ or, $0{\cdot}422$ mole

The above is a quadratic equation hence x may have two values e.g., 1·577 or 0·422. In this example it is impossible to produce more moles of ethyl acetate than the original number of moles of ethanol i.e., 0·5000 mole. So the value 1·577 is improbable. Hence 0·422 moles of $CH_3COOC_2H_5$ must be formed.

∴ Number of moles of CH_3COOH remain unreacted = 1·000 − 0·422 = 0·578 mole.

7. *(a) Calculate equilibrium constant K_p of the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ when 3·85 percent of NH_3 by volume is obtained at equilibrium at 400°C and 10 atmosphere pressure.*

(b) Calculate the total pressure required to give a mixture containing 5% by volume of NH_3 at this temperature.

(c) Calculate the percentage by volume of NH_3 when 3 : 1 mixture of $H_2 : N_2$ is subjected to a pressure of 50 atmosphere.

Ans : (a) [Since 3·85% of NH_3 is formed, of the 96·15% of the unreacted gas, $\frac{1}{4}$ must be N_2 and $\frac{3}{4}$ must be H_2 as the reaction mixture contain 3 : 1 ratio of $H_2 : N_2$]

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{\left(\dfrac{3{\cdot}85}{100} \times 10\right)^2}{\dfrac{1}{4}\left(\dfrac{96{\cdot}15}{100} \times 10\right)\left[\dfrac{3}{4}\left(\dfrac{96{\cdot}15}{100} \times 10\right)\right]^3}$$

$$\text{or, } K_p = 1{\cdot}64 \times 10^{-4}$$

(b) Let P be the total pressure,

$p_{NH_3} = 0{\cdot}05\,P \qquad p_{N_2} = \frac{1}{4}(0{\cdot}95\,P) \qquad p_{H_2} = \frac{3}{4}(0{\cdot}95\,P)$

$$K_p = 1{\cdot}64 \times 10^{-4} = \frac{(0{\cdot}05\,P)^2}{\dfrac{1}{4}(0{\cdot}95\,P)\left[\dfrac{3}{4}(0{\cdot}95\,P)\right]^3} = \frac{0{\cdot}0025\,P^2}{0{\cdot}0859\,P^4}$$

$$\text{or, } P^2 = \frac{0{\cdot}0025}{1{\cdot}64 \times 10^{-4} \times 0{\cdot}0859} = 177{\cdot}5$$

$$P \approx 13{\cdot}3 \text{ atmosphere}$$

(c) According to the equation,
$P_{H_2} = 3P_{N_2}$ and $P_{N_2} + P_{H_2} + P_{NH_3} = 50$ atmosphere or, $P_{NH_3} = 50 - 4P_{N_2}$

$$K_p = 1{\cdot}64 \times 10^{-4} = \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3} = \frac{(50 - P_{N_2})^2}{P_{N_2} \times (3P_{N_2})^3} = \frac{(50 - P_{N_2})^2}{27(P_{N_2})^4}$$

$$\text{or, } \frac{(50 - P_{N_2})^2}{(P_{N_2})^4} = 27 \times 1{\cdot}64 \times 10^{-4}$$

$$\text{or, } \frac{50 - P_{N_2}}{(P_{N_2})^2} = \sqrt{27 \times 1{\cdot}64 \times 10^{-4}} = 0{\cdot}0665$$

or, $P_{N_2} = 10{\cdot}62$ atmosphere
$P_{H_2} = 3 \times 10{\cdot}62 = 31{\cdot}86$ atmosphere
$P_{NH_3} = 50 - (P_{N_2} + P_{H_2}) = 50 - (10{\cdot}62 + 31{\cdot}86) = 7{\cdot}52$ atmosphere

$$\% \, NH_3 = \frac{7{\cdot}52 \times 100}{50} = 15{\cdot}04$$

8. *The equilibrium constant of the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 630 at 490°C. Find at what pressure 50% of N_2O_4 would be dissociated ?*

Ans :

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Number of moles of the start	1		0
At equilibrium, according to the condition, the number of mole	0·5		1

Total number of moles at equilibrium = 0·5 + 1 = 1·5
Let P be the required pressure when 50% N_2O_4 is dissociated.

$$P_{N_2O_4} = \frac{0{\cdot}5}{1{\cdot}5}P \qquad P_{NO_2} = \frac{1}{1{\cdot}5}\cdot P \quad \text{where P = total pressure}$$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{\left(\frac{P}{1{\cdot}5}\right)^2}{\frac{0{\cdot}5}{1{\cdot}5}\cdot P} = \frac{P^2}{1{\cdot}5 \times 1{\cdot}5} \times \frac{1{\cdot}5}{0{\cdot}5 \times P} = \frac{P}{0{\cdot}75}$$

$$\text{or, } 630 = \frac{P}{0{\cdot}75}$$

or, P = 630 × 0·75 = 472·5 atmosphere

9. *One mole of N_2 is mixed with three moles of H_2 in a 4 litre container. If 0.25% N_2 is converted into NH_3 by the following reaction* $N_2 + 3H_2 \rightleftharpoons 2NH_3$
calculate equilibrium constant (K_c) in concentration unit. What will be the value of K_c for the following equilibrium $\frac{1}{2}\,N_2 + \frac{3}{2} \rightleftharpoons NH_3$ *[I.I.T. 1981]*

Ans :

	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
Initial moles	1		3		0
Equil moles	$(1-0{\cdot}0025)$		$(3-0{\cdot}0075)$		$(2\times0{\cdot}0025)$
Equil Conc.	$\frac{1-0{\cdot}0025}{4}$		$\frac{3-0{\cdot}0075}{4}$		$\frac{2\times0{\cdot}0025}{4}$

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

$$K_c = \frac{\left(\frac{2\times 0{\cdot}0025}{4}\right)^2}{\left(\frac{1-0{\cdot}0025}{4}\right)\left(\frac{3-0{\cdot}0025}{4}\right)^3} = 1{\cdot}5 \times 10^{-5}$$

For the second reaction let K_c' be the equilibrium constant—

$$K_c' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$$

$$K_c' = \sqrt{K_c} = \sqrt{1{\cdot}5 \times 10^{-5}}$$

$$K_c' = 3{\cdot}87 \times 10^{-3}\ \text{moles/litre}$$

10. *At a certain temperature equilibrium constant (K_c) is 16 for the reaction.*

$$SO_2(g) + NO_2(g) \leftrightharpoons SO_3(g) + NO(g)$$

If we take 1 mole of each of all the four gases in a one litre container, what would be the equilibrium concentration of NO and NO_2? *[I.I.T. 1987]*

Ans : Let the number of moles of NO_2 that reacts at equilibrium be x. Initial concentration of each gas = 1 mole.

$$\underset{1-x}{SO_2} + \underset{1-x}{NO_2} \rightleftharpoons \underset{1+x}{SO_3} + \underset{1+x}{NO}$$

$$K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} = 16 \quad \text{or,} \quad \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16$$

$$\text{or,} \quad \frac{(1+x)^2}{(1-x)^2} = 16 \quad \text{or,}\ x = 0{\cdot}6$$

$[NO_2]_{\text{equilibrium}} = 1-x = 1-0{\cdot}6 = 0{\cdot}4$ mole

$[NO]_{\text{equilibrium}} = 1+x = 1+0{\cdot}6 = 1{\cdot}6$ moles

Thus, equilibrium mixture contains 0·4 mole of NO_2 and 1·6 moles of NO.

11. *For the reaction, $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, hydrogen gas is introduced into a five litre flask at 327°C containing 0·2 mole of CO(g) and a catalyst, until the pressure is 4·92 atm. At this point 0·1 mole of $CH_3OH(g)$ is formed. Calculate the equilibrium constants, K_p and K_c.* *[I.I.T. '90]*

Ans : Let the total number of moles of all gases at equilibrium point = N. Here pressure P = 4·92 atm. Volume V = 5 litre, $R = 0{\cdot}082\ l\ atm\ mole^{-1}\ K^{-1}$. temperature $T = 273 + 327 = 600$ K.

applying $PV = nRt$.

$$N = \frac{PV}{RT} = \frac{4{\cdot}92 \times 5}{0{\cdot}082 \times 600} = 0{\cdot}5\ \text{moles.}$$

No. of moles of CH_3OH = 0·1 (given)

∴ No. of moles of CO = 0·1

Hence No of moles of $H_2 = 0{\cdot}5 - (0{\cdot}1 + 0{\cdot}1) = 0{\cdot}3$

$$\therefore [CH_3OH] = [CO] = \frac{0{\cdot}1}{5} = 0{\cdot}02, \qquad [H] = \frac{0{\cdot}3}{5} = 0{\cdot}06$$

$$\therefore K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0{\cdot}02}{0{\cdot}02 \times (0{\cdot}06)^2} = 277{\cdot}8\ l^2\ mole^{-2}$$

$$K_p = K_c(RT)^{\Delta n} = 277{\cdot}8 \times (0{\cdot}082 \times 600)^{-2}\ [\because n = (1-3) = -2]$$

$$\text{or } K_p = \frac{277{\cdot}8}{(0{\cdot}082 \times 600)^2} = 0{\cdot}1148\ atm^{-2}$$

12. *0·15 mole of CO is taken in a 2·5 l flask at 750 K along with a catalyst so that the following reaction can take place. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$. H_2 is introduced until the pressure of the system is 8·5 atm. at equilibrium and 0·08 moles of methanol*

is formed Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place.

Ans : Total No. of moles present $N = \frac{PV}{RT} = \frac{8{\cdot}5 \times 2{\cdot}5}{0{\cdot}082 \times 750} = 0{\cdot}35$

No. of moles of CO = 0·15 − 0·08 = 0·07

No. of moles of CH_3OH = 0·08

No. of moles of H_2 = 0·35 − (0·08 + 0·07) = 0·2.

$[CH_3OH] = 0{\cdot}08/2{\cdot}5 = 0{\cdot}032$; $[CO] = 0{\cdot}07/2{\cdot}5 = 0{\cdot}028$, $[H_2] = 0{\cdot}2/2{\cdot}5 = 0{\cdot}08$

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0{\cdot}032}{0{\cdot}028 \times (0{\cdot}08)^2} = 178{\cdot}6\, l^2 \text{mole}^{\;\;2}$$

$K_p = K_c\,(RT)^{\Delta n} = 178{\cdot}6 \times (0{\cdot}082 \times 750)^{-2} = 4{\cdot}71 \times 10^{-2}\ \text{atm}^{-2}$

(ii) Here the total No. of moles = 0·15 + 0·2 + 2 × 0·08 = 0·51. $P = NRT/V$ = (0·51 × 0·082 × 750)/2·5 = 12·546 atm.

• Exercises •

1. What is a reversible reaction ? Explain giving examples. *[H.S. '93]*

2. Explain what is meant by chemical equilibrium ? Explain with an example why the chemical equilibrium is referred to as 'dynamic'. *[Jt. Ent. '83] [H.S. '89, '92, '93]*

3. Show how a state of chemical equilibrium is attained by a system. What are the characteristics of a chemical equilibrium state ?

4. State and explain the law of mass action. What do you understand by the active mass of a substance. Derive a mathematical expression for the equilibrium constant of a homogeneous reversible reaction. *[H.S. '88] [Jt. Ent. '84]*

5. (a) Define equilibrium constant of a reversible reaction ? *[H.S. '92]*

(b) Deduce a relation between K_p and K_c. What is the difference between K_p and K_c ? *[Jt. Ent. '82]*

6. Deduce the equilibrium constant of the following reversible reactions.

(a) $2A + B \rightleftharpoons 3C + D$; (b) $mA + nB \rightleftharpoons pC + qD$.

7. Write down the equation of equilibrium constant K_c for the reversible reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ + 25000 cals.

State whether the arithmetical value of K_c for above reaction will decrease, increase or remain the same, in the following cases, if ;

(i) Only the temperature of the system at equilibrium is increased, keeping other factors constant.

(ii) Only the pressure on the system at equilibrium is increased, keeping temperature and concentration constant.

(iii) A suitable catalyst is introduced into the system keeping temperature, pressure and concentration constant. Mention the possible changes of any type in cases (ii) and (iii). Give reasons for your answers in all the cases. *[Jt. Ent. '81]*

8. Deduce the relations between K_p and K_c for the following reactions—

(a) $2SO_2 + O_2 \rightleftharpoons 2SO_3$; (b) $N_2 + O_2 \rightleftharpoons 2NO$.

9. The equilibrium constant of the reaction $A + B \rightleftharpoons C$ is K_l and that of $M + N \rightleftharpoons P$ is K_2. Find the equilibrium constant for the reaction $A + B + M + N \rightleftharpoons C + P$.

10. Explain the application of the law of mass action for the synthesis of nitric oxide from its elements with special reference to the effect of pressure. *[Jt. Ent. '83]*

11. At a certain temperature and pressure, at the equilibrium of the reversible reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$. 60% NH_3 and 40% N_2 and H_2 are found to be present in the system. Find the percentage of NH_3, N_2 and H_2 when NH_3 is decomposed to form N_2 and H_2 at the same temperature and pressure.

12. State Le Chatelier's principle and hence explain the effects of temperature and pressure on the equilibrium of the reaction represented by the equation $N_2 + 3H_2 \rightleftharpoons 2NH_3$ + 22000 cal. Express the equilibrium constants of the above reaction in terms of K_c and K_p and find out the relation between the two constants. *[Jt. Ent. '82]*

13. Apply Le Chatelier's principle to find out the effect of temperature and pressure on the yield in the Haber's process of synthesis of ammonia. *[Jt. Ent. '87]*

14. State Le Chatelier's principle. Explain its application to find out the effects of temperature, pressure and excess of O_2 on the yield of SO_3 at equilibrium in the contact process for the manufacture of H_2SO_4 from SO_2 and O_2. *[Jt. Ent. '90]*

15. Explain the application of Le Chatelier's principle to find out the effects of temperature, pressure and excess of air on the yield of NO at equilibrium in the Ostwald process of manufacture of nitric acid.

16. What will be the effect of the rate of reaction if the concentration of the reactants is doubled in the following reversible reaction ?

$$H_2 + I_2 \rightleftharpoons 2HI$$

17. Write down K_p in terms of x mole fraction of NH_3 and total pressure P for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ and hence show that x increases with P.

18. State giving reasons the effect of pressure at constant temperature on the positions of equilibrium of the following reaction in which the reactants and products are gaseous. $H_2+I_2 \rightleftharpoons 2HI$ [*Jt. Ent. '90*]

19. Ice contracts on melting. State giving reasons the effect of pressure on its melting point.

20. Illustrate the application of Le Chateleir's principle to determine the influence of temperature and pressure on the condition of equilibrium in the following cases—

(i) $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22{\cdot}4$ k cal
(ii) $H_2 + Br_2 \rightleftharpoons 2HBr$ + Heat
(iii) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - 17000$ cal.
(iv) $N_2 + O_2 \rightleftharpoons 2NO - 21{\cdot}6$ k cal/mole

21. At constant temperature explain the influence of (i) change of temperature, (ii) change of pressure, (iii) presence of a catalyst, (iv) addition of an inert gas, on the equilibrium of a reversible reaction which is exothermic.

22. Explain how will the equilibrium of the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ + heat, at a constant temperature, will be influenced by the following—

(i) N_2 is added from outside (ii) the pressure is decreased (iii) more NH_3 is removed from the system (v) an inert gas is added. Will the reaction go to completion if the reaction is carried out in a closed vessel ?

23. Write the expression for equilibrium constant K for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ + heat. State giving reasons whether the value of K will change, if excess nitrogen is used in this reaction. *[W.B.H.S. '83]*

24. In which of the following reactions the value of $K_p = K_c$?
(a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (b) $2SO_2 + O_2 \rightleftharpoons 2SO_3$, (c) $N_2 + O_2 \rightleftharpoons 2NO$ (d) $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

25. Explain the physico-chemical principle in the manufacture of ammonia by synthetic method.

26. Indicate giving reasons, which of the following reactions will go upto completion.

(a) $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$
(b) $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$
(c) $KOH + HCl \rightarrow KCl + H_2O$
(d) $AgNO_3 + HCl \rightarrow AgCl + HNO_3$

27. Find the equilibrium constant of the reaction $2M(g) + N(g) \rightleftharpoons 2P(g)$. The forward reaction is endothermic and M, N and P are in a close vessel at equilibrium at a constant temperature.

Explain how the concentration of P would change with the change of the following conditions—(i) the concentration of M is increased (ii) volume of the container is increased keeping the temperature constant (iii) the temperature is increased keeping the volume constant.

28. State five conditions by which the point of equilibrium of the following reversible reaction can be shifted towards left.

$$PCl_5(g) \rightleftharpoons PCl_2(g) + Cl_2(g)$$

29. The oxidation of ammonia occurs according to the following reversible reaction

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + 305 \text{ k cal.}$$

(i) Find the K_p and K_c of the reversible reaction and deduce a relation between the two.
(ii) Why the reaction is carried out at 700°C ?
(iii) What is the effect of pressure on the yield of NO ?
(iv) What is the effect of temperature on the yield of NO ?
(v) Will the value of K_c change on addition of Pt catalyst ?
(vi) Will the yield of NO decrease or increase on addition of excess of O_2 ?
(vii) Why the mixture of NH_3 and air (O_2) is passed very rapidly over the catalyst ?
(viii) Why the temperature of the products is rapidly decreased ?
(ix) Will the yield of NO decrease or increase or remain same, if an inert gas is introduced into the system without the change of volume ?

30. (i) What do the following values of K_c of a reversible reaction signify ?—

$$K_c = 1,\ K_c > 1,\ K_c < 1.$$

(ii) Does the value of K depend on temperature ? If so how ?
(iii) What is the effect of adding Cl_2 on the system $PCl_5 \rightleftharpoons PCl_3 + Cl_2$?

(iv) Why will there be difference in the results, if $CaCO_3$ is heated in the open and closed vessel ? *[Jt. Ent. '89]*

(v) The reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is exothermic. Then why is the synthesis of ammonia is carried out at higher temperature ? *[Jt. Ent. '92]*

(vi) Why is the reaction $NaOH + HCl \rightarrow NaCl + H_2O$ is irriversible ?

(vii) NH_4Cl dissolves in water with the absorption of heat. What is the effect of temperature on its solubility ?

(viii) The equilibrium constant of the reaction $M + N \rightleftharpoons P + Q$ at a particular temperature is *K*. Find the equilibrium constants of the following reaction at the same temperature.

(a) $P + Q \rightleftharpoons M + N$; (b) $2M + 2N \rightleftharpoons 2P + 2Q$.

31. Explain why—

(i) V_2O_5 is gradually replacing platinum asbestos in the contact process, though the latter is more effective catalyst.

(ii) The mixture of air and NH_3 is passed very rapidly over the catalyst during the manufacture of HNO_3.

(iii) The rate of evaporation of water increases with the decrease in pressure and increase in temperature.

(iv) The reaction $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$; behaves as a reversible reaction in a closed vessel, but not in open vessel.

(v) The numerical value of the equilibrium constant K_c changes with the change of temperature.

(vi) The numerical value of K_c shows how far the reaction proceeds towards completion.

(vii) A chemical equilibrium can be attained from either side of the reaction.

(viii) A chemical equilibrium is a dynamic one—not static.

(ix) All chemical reactions are reversible.

(x) In a reversible reaction if the forward reaction is exothermic, the yield of the product decreases with the increase of temperature.

(xi) When 1 mole of ethyl alcohol and 1 mole of acetic acid are heated in a closed vessel even for a long time, 1 mole of ester and 1 mole of water are never produced. *[W.B.H.S. '90]*

(xii) A reversible reaction never proceeds upto completion.

(xiii) At high temperature (1150°C) silica displaces the more strongly acidic phosphorus pentoxide from calcium phosphate.

32. (a) A salt dissolves in water to form a saturated solution at room temperature with the evolution of heat. State giving reasons the effect of temperature on the solubility of the salt. *[Jt. Ent. '90]*

(b) Describe the effect of pressure on the position of equilibrium at constant temperature of the reaction $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$ – heat.

33. Whether the following statement is true or false ? Support your answer with reasons.

If equilibrium constant for the reaction $A_2 + B_2 \rightleftharpoons 2AB$, is *K*, then for the backward reaction $AB \rightleftharpoons 1/2A_2 + 1/2B_2$, the equilibrium constant *K'* is *1/K*. *[I.I.T. '84]*

34. The reactions $2CO + O_2 \rightleftharpoons 2CO_2$ and $CaCO_3 \rightleftharpoons CaO + CO_2$ are not complete. How the reactions are brought to completion ?

35. $2M\,(g) + N\,(g) \rightleftharpoons 2P\,(g)$

Suppose that the above reaction is endothermic and that at a definite temperature and pressure, M, N, and P are in equilibrium in a closed vessel. Now, if (i) the volume of the vessel be increased keeping the temperature constant, will the amount of P increase or decrease ? (ii) If the temperature be increased, keeping the volume constant, will the yield of P increase ? Give reasons for your answer in each case. *[W.B.H.S. '82]*

36. (a) Why is chemical equilibrium termed 'dynamic equilibrium'.

(b) Write down the relation between K_p and K_c for the reaction $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$.

(c) What is the effect of (i) change of pressure and (ii) continuous removal of NH_3 from the reaction mixture in the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$. *[W.B.H.S. '94]*

37. The solubility of ammonia in water at constant temperature and pressure is decreased in presence of NaOH in solution—how can you explain this phenomenon in the light of chemical equilibrium concept ? *[W.B.H.S. '94]*

38. $N_2 + 3H_2 \rightleftharpoons 2NH_3$. The equilibrium constant of the above reaction is $K_p = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

Find out the value of K_c of the reaction $1/2N_2 + 3/2H_2 \rightleftharpoons NH_3$.

Objective type :

[A] Select the correct answer (answers) :

(1) In the gaseous equilibrium $P + 2Q \rightleftharpoons R$ + heat, the forward reaction is favoured by

(a) low pressure, high temperature, (b) low pressure, low temperature (c) high pressure, low temperature, (d) high pressure, high temperature. [**Ans.** (c)]

(2) For the reaction $H_2\,(g) + I\,(g) \rightleftharpoons 2HI\,(g)$ the equilibrium constant K_p changes with (a) total pressure (b) catalyst (c) amounts of H_2 and I_2 present (d) temperature. [*Ans.* (d)] *[I.I.T. '81]*

(3) The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if — (a) temperature is increased and pressure is kept constant (b) temperature is reduced and pressure is increased (c) both temperature and pressure are increased (d) both temperature and pressure are decreased. [*Ans.* (b)] *[I.I.T. '81]*

(4) For the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$ the forward reaction at constant temperature is favoured by

(a) introducing an inert gas at constant volume,
(b) introducing chlorine gas at constant volume,
(c) introducing an inert gas at constant pressure,
(d) increasing the volume of the container,
(e) introducing PCl_5 at constant volume. [*Ans.* (c) (d) (e)] *[I.I.T. '91]*

(5) When $NaNO_3$ is heated in a closed vessel, O_2 is liberated and $NaNO_2$ is left behind. At equilibrium (a) addition of $NaNO_2$ favours the reverse reaction, (b) addition of $NaNO_3$ favours the forward reaction, (c) increasing temperature favours the forward reaction, (d) increasing pressure favours the forward reaction. [*Ans.* (a) (b) (c)] *[I.I.T. '86]*

(6) The equilibrium $SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$ is attained at 25°C in a closed container and inert gas He is introduced. Which of the following statements are correct ?

(a) concentrations of SO_2Cl_2, SO_2 and Cl_2 change,
(b) more chlorine is formed,
(c) concentration of SO_2 is reduced,
(d) more SO_2Cl_2 is formed. [*Ans.* (c) (d)] *[I.I.T. '89]*

(7) Which of the following cases, does the reaction go farthest to completion ?
(a) $K = 10^2$ (b) 10^{-2} (c) $K = 10$, (d) $K = I$ [*Ans.* (a)] *[MLNR '90]*

(8) For the reaction $Cu\,(s) + 2Ag^+\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + 2Ag\,(s)$ the equilibrium constant K_c is given by—

(a) $\dfrac{[Cu^{2+}][Ag]^2}{[Cu][Ag]^+]^2}$, (b) $\dfrac{[Cu^{2+}][2Ag]}{[Cu^{2+}][2Ag^+]}$, (c) $\dfrac{[Cu^{2+}]}{[Ag^+]^2}$, (d) $\dfrac{[Ag]^+]^2}{[Cu^{2+}]}$ [*Ans.* (c)]

(9) For the gas phase reaction,
$C_2H_4 + H_2 \rightleftharpoons C_2H_6$; $\triangle H = -\,32{\cdot}7$ k cal, is carried out in a vessel. The equilibrium concentration of C_2H_4 can be increased by
(a) increasing temperature (b) decreasing pressure (c) removing some H_2 (d) adding some C_2H_6. [*Ans.* a to d] *[I.I.T. '84]*

(10) The effect of increasing pressure in the $2A + 3B \rightleftharpoons 3C + 2D$ equilibrium is that (a) forward reaction is favoured, (b) backward reaction is favoured (c) neither reaction is favoured (d) none of the above. [*Ans.* (c)]

[B] Fill in the blanks :

(1) The value of K_c —— with the change of temperature.

(2) If the temperature of a system at equilibrium is increased, the equilibrium will shift in the direction which —— heat.

(3) In the Birkland-Eyde process of manufacture of HNO_3 the yield of NO —— with the increase of pressure.

(4) Law of mass action states that the rate at which a substance reacts is proportional to its —— .

(5) An exothermic reaction which proceeds with the decrease in volume will give maximum yield at —— and ——

11

IONIC EQUILIBRIA

11.1. Electrolytes.

Electrolytes are of two types—*strong* and *weak*. Strong electrolytes undergo complete dissociation in aqueous solution while weak electrolytes suffer negligible dissociation in aqueous medium. According to Arrhenius, the electrolytes dissociate completely or incompletely into ions which remain in equilibrium with the undissociated molecules. The law of mass action can be applied in order to study such equilibrium. Let us consider the case of a binary electrolyte MA.

$$MA \rightleftharpoons M^+ + A^-$$

$$K = \frac{[M^+]\cdot[A^-]}{[MA]} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

K = the ionisation or dissociation constant of the electrolyte.

The equation is tested for various electrolytes in order to verify the constancy of the value of K. In the following table the values of K are given for four different electrolytes at different concentrations.

Concentration in moles/litre	**Value of K in KCl soln.**	**Value of K in Na_2SO_4 soln.**	**Value of K in CH_3COOH soln.**	**Value of K in NH_4OH soln.**
0·0005	$3{\cdot}6 \times 10^{-2}$	$2{\cdot}8 \times 10^{-5}$	$1{\cdot}82 \times 10^{-5}$	$1{\cdot}81 \times 10^{-5}$
0·0001	$5{\cdot}0 \times 10^{-2}$	$7{\cdot}9 \times 10^{-5}$	$1{\cdot}81 \times 10^{-5}$	$1{\cdot}80 \times 10^{-5}$
0·005	$10{\cdot}9 \times 10^{-2}$	$74{\cdot}6 \times 10^{-5}$	$1{\cdot}81 \times 10^{-5}$	$1{\cdot}82 \times 10^{-5}$
0·05	$36{\cdot}0 \times 10^{-2}$	1720×10^{-5}	$1{\cdot}82 \times 10^{-5}$	$1{\cdot}81 \times 10^{-5}$

It is evident from the above table that the value of K is constant for the weak electrolytes but not for strong electrolytes. This is because of the fact that the strong electrolytes exist as ions in their aqueous solution but the weak electrolytes contain lower concentration of ions and an appreciable concentration of undissociated molecules in their aqueous solution. Since the value of K is not constant for the strong electrolytes, the equation (1) is used to calculate the value of dissociation constant of weak acids or bases only.

11.2. Degree of dissociation or degree of ionisation (α).

The degree of ionisation is defined as the fraction of the total electrolyte that ionises at equilibrium in solution.

Thus if α mole ionises out of one mole of the dissolved electrolyte, the degree of ionisation is α. If x% of an electrolyte is ionised in the solution, the degree of ionisation is $x/100$. "*The degree of ionisation is α*", means that out of every mole of the electrolyte α mole ionises and (1 − α) mole is left unionised in the solution.

Now the ions act like molecules in depressing the freezing point, elevating the boiling point, lowering the vapour pressure and establishing the osmotic pressure. Thus an electrolyte which gives two ions per molecule exerts twice the normal effect of the solute,—an electrolyte which gives three ions per molecule exerts thrice the normal effect of the solute and so on.

11.3. Ostwald's dilution Law.

The law states that—*at a given temperature the degree of ionisation of a weak electrolyte is inversely proportional to the square root of the concentration of the solution or directly proportional to the square root of the volume of the solution containing one gram mole of the solute.* It further states that, at a constant temperature, a weak electrolyte in solution gets more ionised with the increase of dilution.

- **Mathematical deduction :**

If one mole of MA is dissolved in 'V' litre of solution and if C and α be the molar concentration and degree of ionisation respectively at this dilution,

$$MA \rightleftharpoons M^+ + A^-$$

Amounts at equilibrium :	$(1-\alpha)$ moles	α gm-ion	α gm-ion
Concentration at equilibrium :	$C(1-\alpha)$ moles	$C\alpha$ gm-ion	$C\alpha$ gm-ion
or,	$\frac{(1-\alpha)}{V}$ moles per litre	$\frac{\alpha}{V}$ gm ion litre	$\frac{\alpha}{V}$ gm-ion per litre

Applying law of mass action,

$$K = \frac{[M^+][A^-]}{[MA]} \text{ .... } (1)$$

If MA is a weak acid, K is called ionisation or dissociation constant of the acid and is symbolised as K_a.

Similarly is case of a base BOH

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K = \frac{[B^+][OH^-]}{[BOH]}$$

Here K is called the dissociation constant of the base and is represented as K_b.

Now putting the values in terms of concentrations in (1),

$$K = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If α is small in comparison to 1 i.e., for a weak electrolyte the dissociation is very small. $(1-\alpha) \approx 1$ then,

$$K = C\alpha^2 \quad \text{or, } \alpha = \sqrt{K/C} \text{ ....} (2)$$

$$\text{Again, } K = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V} \text{ as } (1-\alpha) \approx 1;\ K = \alpha^2/V \text{ or, } \alpha = \sqrt{K.V.} \cdots (3)$$

Both the equations (2) and (3) are mathematical expression for the Ostwald's dilution law.

- **Discussion :**

(i) From eq. (2) it is evident that the degree of ionisation (α) must increase with the decrease of concentration. Thus, as the solution becomes more and more dilute the extent of dissociation is more. *Hence at infinite dilution a weak electrolyte behaves like a strong electrolyte.*

(ii) The law is applicable only to weak electrolyte i.e., weak acids, weak bases etc., because in solution of strong electrolyte no dynamic equilibrium exists and in strong electrolytes ionic interference is very high.

11.4. Ionic product of water (K_w).

Kohlrausch and Heydweiller showed from the conductance measurement that pure water may be regarded as a very weak electrolyte dissociating as—

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying law of mass action,

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

K is called the ionisation constant of water.

$$\text{or,} \quad K[H_2O] = [H^+]\ [OH^-]$$

Since $[H_2O]$ is constant at constant temperature and K is also constant, therefore,

$$K[H_2O] = K_w = [H^+]\cdot[OH^-] \quad \text{or,} \quad K_w = [H^+]\cdot[OH^-]$$

The product of ionic concentration $[H^+]\cdot[OH^-]$ is constant at constant temperature. K_w is called *ionic product of water,* because it is equal to the product of the ionic concentrations of the H^+ and OH^- ions of water. Like any equilibrium constant, K_w also depends on temperature. At 298K the value of $K_w = 1\cdot04\times10^{-14}$. With the rise of temperature the value of K_w increases.

Temperature K	273	298	303	313	373
K_w	$0\cdot05\times10^{-14}$	$1\cdot04\times10^{-14}$	$1\cdot89\times10^{-14}$	$3\cdot8\times10^{-14}$	$4\cdot8\times10^{-14}$

The relation between K_w and temperature is given below—

$$\log \frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{2\cdot303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where, ΔH=Heat of ionisation of water, T_1 and T_2 are the temperatures in Kelvin corresponding to the ionic products K_{w_1}, K_{w_2} respectively.

11.5. pH and pOH.

pH and pOH are the two scales of expressing the concentrations of H^+ and OH^- ions respectively in dilute solution. Normally the concentration of H^+ and OH^- ions of dilute solution are expressed in gram eq./litre. A very convenient method was proposed by *Sorensen.* According to him,

$$pH = \log\frac{1}{[H^+]}, \quad \text{or, } pH = -\log[H^+] \quad \text{or, } [H^+] = 10^{-pH}$$

Thus *pH is the negative logarithm to the base 10 of the hydrogen ion concentration in the solution.* Most aqueous solutions have hydrogen ion concentration between 1M and 1×10^{-14}M. These solutions have pH between 0 and 14 and so it is more convenient to express the acidity in terms of pH rather than $[H^+]$. This avoids using negative exponents or fractions.

(i) A neutral solution has pH=7, pure water has pH=7.
(ii) An acidic solution has pH less than 7.
(iii) An alkaline solution has pH greater than 7.

[H]→	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH→	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

←————Acidic————→Neutral←————Alkaline————→

It is observed that the greater the value of $[H^+]$, the smaller will be the value of pH and vice versa. A neutral solution is one in which $[H^+]=[OH^-]$.

In a similar manner, *pOH is the negative logarithm to the base 10 of the OH^- ion concentration in the solution.*

$$\text{pOH} = -\log[OH^-]$$

$$\text{or,}\quad [OH^-] = 10^{-\text{pOH}}$$

We know, $[H^+][OH^-] = K_w = 1 \times 10^{-14}$

Taking log on both sides,

$$\log[H^+] + \log[OH^-] = \log K_w = \log(1 \times 10^{-14})$$

$$\text{or,}\quad -\log[H^+] - \log[OH^-] = -\log K_w = -\log(1 \times 10^{-14})$$

$$\text{or,}\quad \text{pH} + \text{pOH} = \text{p}K_w = 14$$

$$\text{or,}\quad \text{pH} + \text{pOH} = 14.$$

In a neutral solution pH = pOH = 7.

i.e., $[H^+] = [OH^-] = 1 \times 10^{-7}$ gram-ion/litre.

1. *Calculate the pH of 0·1(N) HCl.*

$$\text{pH} = -\log 0{\cdot}1 \qquad \text{or, pH} = 1$$

2. *Calculate the pH of 10^{-8}(N) HCl.*

In this case the dissociation of H_2O is to be taken into account. While calculating the pH of (N/10) HCl (strong acid) we did not consider that.

For (N/10) HCl :

$$HCl \rightleftharpoons H^+ + Cl^-$$

Here $[H^+] = 10^{-1}$ gram-ion/litre

$$H_2O \rightleftharpoons H^+ + OH^-$$

Here $[H^+] = 10^{-7}$ gram-ion/litre

Since in (N/10) HCl, the $[H^+]$ furnished by HCl is 1 million times larger than that furnished by water we can neglect $[H^+]$ which comes from water ; but in calculating the pH of 10^{-8}(N) HCl, the $[H^+]$ from water is 10 times more than that of 10^{-8}(N) HCl.

For 10^{-8}(N) HCl :

$$HCl \rightleftharpoons \underset{\substack{10^{-8}\text{ gram-ion}\\ \text{per litre}}}{H^+} + Cl^-$$

$$H_2O \rightleftharpoons \underset{\substack{10^{-7}\text{ gram-ion}\\ \text{per litre}}}{H^+} + OH^-$$

Hence in this case,

$$\begin{aligned}[H]_{\text{total}} &= [H^+]_{HCl} + [H^+]_{H_2O}\\ &= (10^{-8} + 10^{-7})\text{ gram-ion/litre}\\ &= (0{\cdot}1 + 1) \times 10^{-7}\text{ gram-ion/litre}\\ &= (1{\cdot}1 \times 10^{-7})\text{gram-ion/litre}\end{aligned}$$

$$\begin{aligned}\text{pH} &= -\log(1{\cdot}1 \times 10^{-7})\\ &= 7 - \log 1{\cdot}1 = 7 - 0{\cdot}0414\\ &= 6{\cdot}9586\end{aligned}$$

Hence the pH of 10^{-8}(N) HCl is not 8 but 6·9586—very weakly acidic.

11.6. Buffer Solution.

If 0·01 mole of NaOH be added to 1 litre of a solution of 10^{-4}(N) HCl (pH = 4), all the acid is converted to its salt NaCl and an excess NaOH is left.

$$\begin{aligned}\text{Number of moles of NaOH left unused} &= 0{\cdot}01 - 0{\cdot}0001\\ &= 0{\cdot}0099\text{ mole}\\ &= 9{\cdot}9 \times 10^{-3}\text{ mole}\\ \text{i.e., }[OH^-]\text{ in the resulting solution} &= 9{\cdot}9 \times 10^{-3}\text{ molar}\end{aligned}$$

$$pOH = -\log(9{\cdot}9 \times 10^{-3}) = 3 - \log 9{\cdot}9$$
$$= 3 - 0{\cdot}9956 \approx 2$$
$$\therefore pH = 14 - 2 = 12.$$

Therefore, addition of 0·01 mole of NaOH changes the pH of the solution from 4 to 12.

Again, if we add 0·01 mole of HCl to 1 litre of a solution containing 0·1(N) CH_3COOH and 0·1(N) CH_3COONa, the pH changes from 4·73 to 4·64. Similarly if 0·01 mole of NaOH is added to 1 litre of such solution the pH increases from 4·73 to 4·82. In either case the change of pH is negligible—only 0·09 unit.

Thus, it is evident from above that there are some solutions which can resist the change of pH when acid or alkali is added to it.

The resistance of a solution to change its pH on addition of small quantity of acids (H^+ ions) or alkalis (OH^- ions) is known as buffer action.

- *Buffer solutions are solutions which resist change in their pH value on adding small quantities of acids or alkalis to them. They retain practically a constant pH value.*

A buffer solution is said to possess reserve acidity and reserve alkalinity.

It consists of either *a mixture of weak acid and its salt with strong base* or *a weak base and its salt with strong acid.*

Examples of buffer solution : (i) CH_3COOH and CH_3COONa, (ii) NH_4OH and NH_4Cl, (iii) H_2CO_3 and $NaHCO_3$.

- **pH of buffer solution :**

The pH of a buffer solution is calculated by applying **Henderson's equation.**

Let us consider a buffer solution containing a *weak acid HA and its salt BA (with strong base BOH).*

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{or, } [H^+] = \frac{K_a[HA]}{[A^-]}$$

Taking log on both sides,

$$\log[H^+] = \log K_a + \log\frac{[HA]}{[A^-]}$$

$$\text{or, } -\log[H^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$\text{or, } pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$\text{i.e., } pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$ This is called **Henderson's equation.**

Here salt provides the negative ion A^- which is the conjugate base of the acid HA.

Similarly in *case of mixture of weak base and its salt with strong acid,* the form of Henderson's equation for such buffer is

$$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

- **Buffer action :**

Let us consider an acidic buffer containing a weak acid HA and its salt MA,

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{or,} \quad [H^+] = \frac{K_a[HA]}{[A^-]} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

The salt provides the anion A^- which is the conjugate base of the acid HA.

$$\underset{\text{acid}}{HA} \rightleftharpoons H^+ + \underset{\text{base}}{A^-}$$

From (1) it is evident that pH of the mixture depends upon the ratio of the conjugate acid to the base and not on the individual concentration. Since the ratio does not alter on dilution with water, the $[H^+]$ or pH remains almost constant.

If a small amount of strong acid say H_2SO_4, HCl etc., be added to an acidic buffer, the H^+ ions furnished by the strong acids combine with A^- ion of the salt to form undissociated acid HA. $H^+ + A^- \rightleftharpoons HA$. It shows that [HA] increases slightly and the salt decreases to the same extent. From equation (1), K_a is constant, hence $[H^+]$ or pH remains constant.

On the otherhand, if some strong alkali is added to the above buffer, the OH^- ions furnished by the strong alkali react with the acid to form H_2O and A^- ion.

$$HA + OH^- \rightleftharpoons H_2O + A^-$$

Thus $[A^-]$ increases i.e., the concentration of the salt increases and the concentration of the acid decreases proportionally. As a result $[H^+]$ practically remains constant. Thus the addition of small amount of strong acid or alkali changes the pH of the buffer very little.

- **Buffer capacity :**

The magnitude of the buffer action of a solution is determined by *buffer capacity*. It is defined as the number of moles of acid or base required by one litre of a buffer solution to change its pH by one unit.

Mathematically if dx stands for amount (mole) of acid or base and β (Beta) for the buffer capacity then,

$$\text{Buffer capacity} = \frac{\text{No. of moles of acid or base per litre of buffer}}{\text{Change of } pH} \quad \text{or, } \beta = \frac{dx}{d\,(pH)}$$

Thus buffer capacity is a function of number of moles of acids or alkalies used to prepare a buffer with definite change of *pH*. Higher the number of moles of acids or alkalies used, higher will be the buffer capacity.

[A buffer solution having equal concentration of acid and its corresponding salt or a half neutralised acid has the maximum buffer capacity. In general buffer capacity is maintained for mixture within a range of 1 acid : 10 salt and 10 acid : 1 salt.

The *pH* range of the buffer—

$$pH = pK_a + \log\frac{10}{1} = pK_a + 1 \quad \text{and} \quad pH = pK_a + \log\frac{1}{10} = pK_a - 1$$

$$\text{or, } pH = pK_a \pm 1]$$

- **Example :**

A buffer solution is made of 0·1(M) CH_3COOH and 0·1(M) CH_3COONa. Let us see how much the pH change occurs when 1 ml of 10(N) HCl and 2 ml of 5(N) NaOH are added separately to 1 litre of this buffer. (Given $K_a = 1{\cdot}82 \times 10^{-5}$)

$$\text{Now } pK_a = -\log(1{\cdot}82 \times 10^{-5})$$

$$= 5 - \log 1{\cdot}82 = 5 - 0{\cdot}2601 = 4{\cdot}7399.$$

Applying Henderson equation,

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4{\cdot}7399 + \log\frac{0{\cdot}1}{0{\cdot}1}$$

$$= 4{\cdot}7399.$$

Thus the pH of the buffer is 4·7399.

(i) The $[H^+]$ in 1 ml of 10 (M) HCl $= \dfrac{1 \times 10}{1000} = 0{\cdot}01$ gram-ion/litre.

The H^+ ions from HCl would react with CH_3COO^- to form CH_3COOH.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

[Acid] is thus increased at the proportionate decrease of [Salt].

$$[\text{Salt}] = 0{\cdot}1 - 0{\cdot}01 = 0{\cdot}09 \text{ gram-ion/litre}$$
$$[\text{Acid}] = 0{\cdot}1 + 0{\cdot}01 = 0{\cdot}11 \text{ gram-ion/litre}$$

Now applying Henderson equation,

$$\text{pH} = 4{\cdot}7399 + \log\frac{0{\cdot}09}{0{\cdot}11} \quad \because \ pK_a = 4{\cdot}7399$$
$$\text{or, pH} = 4{\cdot}7399 + \log\frac{9}{11}$$
$$= 4{\cdot}7399 + 0{\cdot}9542 - 1{\cdot}0414 = 4{\cdot}6527$$
$$\approx 4{\cdot}65$$

Thus, the change of pH $= 4{\cdot}74 - 4{\cdot}65 = 0{\cdot}09$ unit.

(ii) $[OH^-] = \dfrac{2 \times 5}{1000} = 0{\cdot}01$ gram-ion/litre

OH^- ions combine with CH_3COOH to form salt.

$$OH^- + CH_3COOH \rightarrow CH_3COO^- + H_2O$$

Thus [Salt] is increased while [Acid] is proportionately decreased.

$$[\text{Acid}] = 0{\cdot}1 - 0{\cdot}01 = 0{\cdot}09 \text{ gram-ion/litre}$$
$$[\text{Salt}] = 0{\cdot}1 + 0{\cdot}01 = 0{\cdot}11 \text{ gram-ion/litre}$$

$$\text{pH} = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = 4{\cdot}7399 + \log\frac{0{\cdot}11}{0{\cdot}09}$$
$$= 4{\cdot}7399 + \log\frac{11}{9} = 4{\cdot}7399 + 1{\cdot}0414 - 0{\cdot}9542$$
$$= 4{\cdot}8271 \approx 4{\cdot}83$$

Thus, pH is increased by $4{\cdot}83 - 4{\cdot}74 = 0{\cdot}09$ unit.

- **Some commonly used buffer and their pH range.**

Composition	pH range
1. Acetic acid + Sodium acetate	3·7 – 5·6
2. Borax + Boric acid	6·8 – 9·2
3. Ammonium hydroxide + Ammonium chloride	8·5 – 10·8
4. Na H_2PO_4 + Na_2HPO_4	4·0 – 6·2
5. Phthalic acid + Potassium hydrogen phthalate	2·2 – 3·8

• Application of buffers :

(i) **In biochemistry** : Blood and various other human fluids are highly buffered with bicarbonate, carbonic acid and proteins. pH of human blood is 7·4—slightly alkaline. If the pH of blood falls to 7 or rise to 7·7, the result may be fatal. Due to the buffering action of H_2CO_3 and $NaHCO_3$ the pH of blood is maintained constant.

Rates of various enzymatic reactions in human body are controlled by natural buffers.

(ii) **In chemical analysis** : Buffer solutions of different pH values are used in the qualitative and quantitative analysis e.g., (a) Fe^{+++}, Cr^{+++} and Al^{+++} are precipitated in Gr III A as hydroxides by adding NH_4Cl and NH_4OH. This mixture acts as a buffer.

(b) The stability of metal—E.D.T.A. complex is controlled by constant pH. Hence in complexometric titration of metal ions with E.D.T.A., it is essential to maintain the pH of the resulting solution constant.

(iii) **In the separation of PO_4^{3-} by $FeCl_3$** method, a buffer of glacial acetic acid and CH_3COONH_4 is used which maintains a constant pH of 4·6. $FePO_4$, $CrPO_4$ and $AlPO_4$ are insoluble in this buffer while the phosphates of Gr III B, IV and Mg are soluble in it.

(iv) **In Agriculture :** In the preservation of fruits and fruit products suitable buffers are used. pH of the soil is very important for the healthy growth of crops and seeds.

(v) Buffer solutions are used in medicine and in many industrial processes e.g., dying, paper, inks, tanning of leather, in fermentation industry etc.

11.7. Hydrolysis of salts.

We know that acids react with bases to produce salts. A normal salt should be neutral in water, but sometimes they exibit acidic or alkaline reaction in aqueous medium. The inter action of salts with water to give basic or acidic solution is called *hydrolysis*. As a result of hydrolysis the normal salts form acids or alkalis that neutralise each other to form that salt. Hence *hydrolysis may be looked upon as a reverse reaction of neutralisation*.

- *Hydrolysis is the inter action between the cation or anion of the salt and the H^+ and OH^- ions of water to form (i) either a weak acid or a weak base, (ii) both a weak acid and a weak base. The resulting solution becomes either weakly acidic or weakly basic.*

Four types of salts are normally found—

(i) Salts of strong acid and strong base e.g., NaCl, KNO_3, etc.
(ii) Salts of strong acid and weak base e.g:, NH_4Cl, $FeCl_3$, $CuSO_4$ etc.
(iii) Salts of weak acid and strong base e.g., Na_2CO_3, CH_3COONa etc.
(iv) Salts of weak acid and weak base e.g., $(NH_4)_2CO_3$, CH_3COONH_4 etc.

1. Salts of strong acid and strong base : Let the salt MA is derived from strong acid HA and strong base MOH e.g., NaCl. When such type of salt is dissolved in water, it yields the strong acid HA and strong base MOH.

$$MA + H_2O \rightarrow HA + MOH$$

As both the acid (HA) and alkali (MOH) are strong, they would ionise completely and the concentration of H^+ and OH^- ions in the solution being same, the final solution will be neutral. The pH of such solution will be 7. Therefore, neither the original acid nor the original base is regenerated. Hence the salts of strong acid and strong base do not hydrolyse at all.

2. Salts of strong acid and weak base (*Cationic hydrolysis*) : $FeCl_3$, $AlCl_3$, NH_4Cl, $CuSO_4$, $FeSO_4$ etc., belong to this type of salts. An aqueous solution of all such salts are acidic in nature.

(i) NH_4Cl is a salt of HCl (strong acid) and NH_4OH (weak base). It is hydrolysed to generate both HCl and NH_4OH.

$$NH_4Cl + H_2O = H^+ + Cl^- + NH_4OH$$

HCl is strong acid, so it dissociates completely in aqueous solution.

NH_4OH is a weak base—it dissociates incompletely. Therefore, the concentration of H^+ ions becomes more than that of OH^- ions furnished by NH_4OH. Hence the resulting solution becomes acidic. pH of such solution is less than 7. This type of hydrolysis is called cationic hydrolysis, since the cation of the salt e.g., NH_4^+ disturbs the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ of water by forming practically undissociated weak electrolyte NH_4OH. As a result, the equilibrium is shifted towards the right, enhancing the concentration of H^+ ions. Consequently the final solution becomes acidic.

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

(ii) Hydrolysis of $FeCl_3$.

$FeCl_3$ is hydrolysed by water to generate HCl (strong acid) and $Fe(OH)_3$ (weak base).

$$FeCl_3 + 3H_2O \rightleftharpoons 3\,(H^+ + Cl^-) + Fe(OH)_3$$

HCl being strong dissociates completely while $Fe(OH)_3$ being weak dissociates incompletely in aqueous medium.

As $[H^+] > [OH^-]$, the final solution becomes acidic. The cation Fe^{+++} disturbs the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ forming practically undissociated $Fe(OH)_3$ enhancing the concentration of H^+ ions.

$$Fe^{+++} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

The increase of H^+ ion concentration leads to the acidity of the resulting solution.

This type of hydrolysis is called *cationic hydrolysis. Cationic hydrolysis makes the aqueous solution acidic.*

- **When an aqueous solution of Na_2CO_3 is added to an aqueous solution of $FeCl_3$ or $AlCl_3$, the corresponding carbonates are not precipitated—Explain why.**

This is because of the fact that $FeCl_3$ or $AlCl_3$ undergoes hydrolysis to generate HCl (strong acid) and weak base $Fe(OH)_3$ or $Al(OH)_3$. The liberated HCl attacks Na_2CO_3 liberating CO_2 and precipitating the corresponding hydroxides shifting the equilibrium to the right.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3\downarrow + 3H^+ + 3Cl^-$$
$$Na_2CO_3 + 2H^+ + 2Cl^- = 2NaCl + CO_2\uparrow + H_2O$$

- **Degree of hydrolysis :**

The degree of hydrolysis of a salt is defined as the fraction of the total salt that hydrolyses at equilibrium in the solution. The degree of hydrolysis of a salt is '*h*'—it means that, out of 1 mole of the salt taken, *h* mole undergoes hydrolysis and $(1-h)$ mole of the salt is left unhydrolysed at equilibrium. If a salt is hydrolysed by $x\%$, the degree of hydrolysis is $x/100$.

Quantitative evaluation :

Let us consider a salt MA which is formed by the action of strong acid HA with weak base MOH. Let the degree of hydrolysis and concentration be *h* and C respectively. The general equation of hydrolysis of second type of salts is—

$$\begin{array}{ccccccccc} M^+ & + & A^- & + & H_2O \rightleftharpoons MOH & + & H^+ & + & A^- \\ & & M^+ & + & H_2O \rightleftharpoons MOH & + & H^+ & & \\ & & C(1-h) & & \quad Ch & & Ch & & \end{array}$$

Applying the law of mass action,

$$K_h = \frac{[H^+][MOH]}{[M^+][H_2O]}$$

Since the active mass of H_2O is constant,

$$K_h = \frac{[H^+][MOH]}{[M^+]}$$

K_h is called the hydrolysis constant.

$$K_h = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since *h* is very small $(1-h) \approx 1$

$$\text{or,} \quad K_h = Ch^2$$

There are also two other equilibria in the solution.

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$K_w = [H^+][OH^-]$$

$$MOH \rightleftharpoons M^+ + OH^-$$

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

$$\frac{K_w}{K_b} = \frac{[H^+][OH^-][MOH]}{[M^+][OH^-]} = \frac{[H^+][MOH]}{[M^+]} = K_h$$

$$\text{or, } K_h = \frac{K_w}{K_b}$$

Thus *hydrolysis constant is the ratio of the ionic product of water to the dissociation constant of the weak base MOH.*

$$\frac{K_w}{K_b} = K_h = Ch^2$$

$$\text{or, } h = \sqrt{\frac{K_w}{K_b C}}$$

$$\text{Again } Ch = \sqrt{\frac{K_w . C}{K_b}} \quad \text{or, } [H^+] = \sqrt{\frac{K_w . C}{K_b}}$$

Taking log on both sides,

$$\log [H^+] = \tfrac{1}{2}[\log K_w + \log C - \log K_b]$$

$$-\log [H^+] = -1/2 \log K_w - 1/2 \log C + 1/2 \log K_b$$

$$\text{or, } \quad pH = 1/2\, pK_w - 1/2\, pK_b - 1/2 \log C.$$

$$pK_w = 14.$$

$$\therefore \quad pH = 7 - \tfrac{1}{2}(pK_b + \log C)$$

This equation confirms that during cation hydrolysis the pH of the resulting solution must be less than 7 i.e., acidic (pK_b = positive integer).

(3) Salt of strong base and weak acid (anionic hydrolysis) :

Salts like Na_2CO_3, KCN, CH_3COONa, KBO_2 etc., are produced by the action of strong base with weak acid. They exhibit alkaline reaction on hydrolysis.

(i) Hydrolysis of KCN.

KCN is a salt of weak acid HCN and strong base KOH. It is hydrolysed to produce KOH and HCN.

$$KCN + H_2O \rightleftharpoons [K^+ + OH^-] + HCN$$

KOH is strong base, so it dissociates completely in aqueous solution. HCN is a weak acid—so it dissociates incompletely. Therefore $[OH^-] > [H^+]$ per unit volume of the solution and so the resulting solution becomes alkaline.

Such type of hydrolysis is called anionic hydrolysis since the anion of the salt e.g., CN^- disturbs the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ of water by forming practically undissociated weak acid HCN. As a result, the equilibrium is shifted towards the right enhancing the concentration of OH^- ions, as a result of which the solution becomes alkaline

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

Anionic hydrolysis makes the aqueous solution alkaline. pH of such solution is always greater than 7.

(ii) Hydrolysis of Na_2CO_3 :

It is a salt of strong base NaOH and weak acid H_2CO_3. It undergoes hydrolysis to produce strong base NaOH and weak acid H_2CO_3.

$$Na_2CO_3 + H_2O \rightleftharpoons 2(Na^+ + OH^-) + H_2CO_3$$

NaOH is a strong base, so it dissociates completely in aqueous solution. H_2CO_3 is a weak acid, so it dissociates incompletely. Since $[OH^-]>[H^+]$, the resulting solution is alkaline. The anion CO_3^{--} disturbs the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ of water by forming practically undissociated weak H_2CO_3. Consequently the equilibrium is shifted towards the right enhancing the concentration of OH^-. So the final solution becomes alkaline.

$$CO_3^{--} + 2H_2O \rightleftharpoons H_2CO_3 + 2OH^-$$

Quantitative evaluation :

$$M^+ + A^- + H_2O \rightleftharpoons M^+ + OH^- + \underset{\text{weak acid}}{HA}$$

$$\underset{C(1-h)}{A^-} + H_2O \rightleftharpoons \underset{C.h}{HA} + \underset{C.h}{OH^-}$$

Let h be the degree of hydrolysis and C be the concentration of the salt MA which is formed by the action of strong base MOH with weak acid HA. The base MOH being strong, completely ionises and acid HA being weak remains almost undissociated.

Applying the law of mass action,

$$K_h = \frac{[HA][OH^-]}{[A^-][H_2O]}$$

The active mass of water is constant.

$$\therefore K_h = \frac{[HA][OH^-]}{[A^-]} = \frac{C.h \times C.h}{C(1-h)} = \frac{C.h^2}{1-h}$$

Since h is very small $(1-h) \approx 1$

$$K_h = C.h^2 \quad \text{or,} \quad h = \sqrt{\frac{K_h}{C}}$$

K_h is hydrolysis constant.

There are also two other equilibria in the solution.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][OH^-], \quad K_w = \text{ionic product of water}$$

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad K_a\text{=ionisation constant of weak acid HA.}$$

$$K_w/K_a = \frac{[H^+][OH^-][HA]}{[H^+][A^-]} = \frac{[HA][OH^-]}{[A^-]} = K_h$$

$$\text{or,} \quad K_h = K_w/K_a$$

Hydrolysis constant K_h is thus the ratio of the ionic product of water to the dissociation constant of the weak acid HA.

Again, $K_h = C.h^2 = K_w/K_a$

$$\text{or,} \quad h = \sqrt{\frac{K_w}{K_a.C}}$$

$$\text{Now} \quad [OH^-] = C.h = C\sqrt{\frac{K_w}{K_a.C}} = \sqrt{\frac{K_w.C}{K_a}}$$

$$\text{or,} \quad [OH^-] = \sqrt{\frac{K_w.C}{K_a}} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\text{Again } [H^+][OH^-] = K_w \quad \text{or,} \quad [OH^-] = K_w/[H^+] \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

From (1) and (2) we get, $\frac{1}{[H^+]} = \sqrt{\frac{C}{K_w . K_a}}$

Taking log on both sides,

$$\log 1 - \log [H^+] = \tfrac{1}{2}[\log C - \log K_w - \log K_a]$$

or, $pH = \frac{1}{2}\log C + \frac{1}{2}pK_w + \frac{1}{2}pK_a$ since $1/2\, pK_w = 7$

$$pH = 7 + 1/2\, pK_a + 1/2 \log C.$$

pK_a is a positive integer, hence pH must be greater than 7 i.e., the resulting solution will be alkaline.

4. Salts of a weak acid and a weak base :

In this case unless some parameter is known, it is not possible to predict whether after hydrolysis, the resulting solution will have pH=7, or >7 or, <7. This is because of the fact that, in this case both the acid and the base are weak and unless the degree of dissociation or pK_a or pK_b values are known, it is not possible to predict the nature of the resulting solution after hydrolysis. Salts like $(NH_4)_2CO_3$, CH_3COONH_4, $(CH_3COO)_2Pb$ etc., belong to this category.

(i) Hydrolysis of CH_3COONH_4 :

It is a salt of weak acid CH_3COOH and weak base NH_4OH. Both CH_3COOH and NH_4OH being weak electrolyte, dissociate incompletely in aqueous solution.

$$\begin{aligned} CH_3COOH &\rightleftharpoons CH_3COO^- + H^+ \\ NH_4OH &\rightleftharpoons NH_4^+ + OH^- \end{aligned}$$

The resulting solution may be neutral, acidic or alkaline as to whether $[H^+] = [OH^-]$ or, $[H^+] > [OH^-]$ or, $[H^+] < [OH^-]$

Let α_1 = degree of ionisation of CH_3COOH
α_2 = degree of ionisation of NH_4OH

Now if $\alpha_1 = \alpha_2$ the resulting solution will be neutral
if $\alpha_1 > \alpha_2$ the resulting solution will be acidic
if $\alpha_1 < \alpha_2$ the resulting solution will be alkaline.

In this particular case $\alpha_1 = \alpha_2$, hence the aqueous solution of $CH_3COO\,NH_4$ will be neutral.

(ii) Hydrolysis of $(NH_4)_2CO_3$ solution :

$$\begin{aligned} (NH_4)_2CO_3 &\rightleftharpoons 2NH_4^+ + CO_3^{--} \\ 2H_2O &\rightleftharpoons 2H^+ + 2OH^- \\ \hline (NH_4)_2CO_3 + 2H_2O &\rightleftharpoons 2NH_4OH + H_2CO_3 \end{aligned}$$

Let α_1 = degree of ionisation of NH_4OH and α_2 = degree of ionisation of H_2CO_3. Here, $\alpha_1 > \alpha_2$ hence the resulting solution be alkaline.

Quantitative evaluation :

In this case both cations and anions of the salt could be hydrolysed but the products would remain undissociated.

$$\underset{C(1-h)}{M^+} + \underset{C(1-h)}{A^-} + H_2O \rightleftharpoons \underset{C.h}{MOH} + \underset{C.h}{HA}$$

C = concentration of the salt, and h = degree of hydrolysis.

$$K_h = \frac{[MOH][HA]}{[M^+][A^-]}$$

In addition to the above equilibrium there are three other equilibria in the solution.

$$H_2O \rightleftharpoons H^+ + OH^- \,;\, K_w = [H^+][OH^-]$$

$$MOH \rightleftharpoons M^+ + OH^- ; K_b = \frac{[M^+][OH]^-}{[MOH]}$$

$$HA \rightleftharpoons H^+ + A^- ; \; K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\text{or,} \quad \frac{K_w}{K_a . K_b} = \frac{[H^+][OH^-][MOH][HA]}{[M^+][OH^-][H^+][A^-]} = \frac{[MOH][HA]}{[M^+][A^-]} = K_h$$

$$\text{or,} \; K_h = \frac{C.h \times C.h}{C(1-h) . C(1-h)} = \frac{h^2}{(1-h)^2}$$

$$\text{or,} \; \sqrt{K_h} = \frac{h}{(1-h)}$$

Again $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{or,} \; [H^+] = \frac{K_a [HA]}{[A^-]}$$

Since $[HA] = C.h$ and $[A^-] = C(1-h)$

$$[H^+] = \frac{K_a \times C.h}{C(1-h)} = \frac{K_a h}{(1-h)} = K_a \sqrt{K_h}$$

Substituting the value of $K_h = \frac{K_w}{K_a . K_b}$ we get,

$$[H^+] = K_a \sqrt{\frac{K_w}{K_a K_b}} \quad \text{or,} \; [H^+] = \sqrt{\frac{K_w . K_a}{K_b}}$$

Taking log on both sides,

$$\log [H^+] = 1/2 [\log K_w + \log K_a - \log K_b]$$

$$\text{or,} \quad -\log [H^+] = -1/2 \log K_w - 1/2 \log K_a + 1/2 \log K_b$$

$$\text{or,} \quad pH = 1/2\, pK_w + 1/2\, pK_a - \tfrac{1}{2}\, pK_b$$

$$\text{or,} \quad pH = 7 + 1/2\, pK_a - 1/2\, pK_b$$

In this case the pH of the solution is independent of the concentration of the salt.

Here three cases may arise :

(a) If $pK_a = pK_b$ then pH=7, i.e., the resulting solution will be neutral.

(b) If $pK_a < pK_b$ i.e., acid is stronger than the base the resulting solution will be acidic.

(c) If $pK_a > pK_b$ then pH is greater than 7, the resulting solution will be alkaline.

- **Hydrolysis of acid salts :**

Explain why the aqueous solution of $NaHSO_4$ is acidic and $NaHCO_3$ is alkaline.

Acid salts undergo hydrolysis and the acidic or alkaline nature of the resulting solution depends upon the nature of the hydrolysis.

Thus an aqueous solution of $NaHSO_4$ is acidic, as it gives HSO_4^- ions in aqueous medium.

$$NaHSO_4 \rightleftharpoons Na^+ + HSO_4^-$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{--}$$

Since the $[H_3O^+]$ is increased, the resulting solution is acidic.

An aqueous solution of $NaHCO_3$ is alkaline as it gives OH^- ions in aqueous medium.

$$NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

Insoluble salts like AgCl, Cu_2Cl_2, Hg_2Cl_2 etc., do not hydrolyse at all.

• Difference between Neutralisation and Hydrolysis •

Hydrolysis	Neutralisation
1. Hydrolysis is the reaction in which cation or anion of the salt reacts with H^+ or OH^- ions of water to form an acid or a base or both an acid and a base.	1. Neutralisation amounts to the formation of undissociated water molecule by the interaction between H^+ and OH^- furnished by acid and base respectively.
2. Hydrolysis is reversible process and is never complete.	2. Neutralisation is an irreversible process and is mostly complete.
3. The extent of hydrolysis is controlled by the concentration of the salt (except salt of weak acid and weak base).	3. Neutralisation is independent upon the concentration of the acid or alkali.
4. Three types of salts are hydrolysed. A salt formed from strong acid and strong base does not hydrolyse.	4. Neutralisation occurs whether the acid or base is strong or weak. Hence four types of salts are known.

11.8. Indicators.

Three types of indicators are commonly used—(i) *acid-base indicator*, (ii) *redox indicator* and (iii) *adsorption indicator*. A brief discussion of the theory of acid-base indicator is presented here.

In order to explain the mechanisim of indicator two theories are put forward—

(A) **The Ostwald acid-base theory.**

(B) **The Quinonoid theory.**

[A] Ostwald acid-base theory :

(i) All acid- base indicators are either weak organic acids or weak organic bases. The ionised and unionised forms of indicators have different colours.

(ii) Colour of the acid-base indicator is due to the ion given by it in solution.

(iii) Change of colour of the indicator is attributed to the change of pH of the medium.

(iv) Acidic indicators show deep colour in basic medium while basic indicators show deep colour in acidic medium.

Representing an acid indicator as HIn and basic indicator as InOH.

$$\underset{\substack{\text{unionised}\\ \text{form}}}{HIn} \rightleftharpoons H^+ + \underset{\substack{\text{ionised}\\ \text{form}}}{In^-} \quad \cdots\cdots(1)$$

$$\underset{\substack{\text{unionised}\\ \text{form}}}{InOH} \rightleftharpoons \underset{\substack{\text{ionised}\\ \text{form}}}{In^+} + OH^- \quad \cdots\cdots(2)$$

HIn and In^- have different colours, so also InOH and In^+

Applying law of mass action in equilibrium (1),

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \qquad K_{In} = \text{Indicator constant.}$$

$$[H^+] = \frac{K_{In} \times [HIn]}{[In^-]}$$

$$\text{or,} \quad \log[H^+] = \log K_{In} + \log\frac{[HIn]}{[In^-]}$$

$$\text{or, } -\log[H^+] = -\log K_{In} - \log \frac{[HIn]}{[In^-]}$$

$$\text{or, } pH = pK_{In} + \log \frac{[In^-]}{[HIn]} \cdots\cdots (3)$$

$$\text{or, } pH = pK_{In} + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

Thus, the colour of the indicator is determined by the ratio $\frac{[In^-]}{[HIn]}$ and is dependent of pH. Equation (3) is analogous to Henderson's equation.

When $[HIn] = [In^-]$, $pH = pK_{In}$

So indicator constant K_{In} is equal to $[H^+]$ at which the change in colour of the indicator is half completed.

For any indicator pK_{In} is constant. Hence it follows from (3) whenever the pH of the solution is changed, the ratio $\frac{[In^-]}{[HIn]}$ must also be changed.

Now in a bicolour system (say blue and yellow), blue colour will still be perceived by normal eye along with the yellow if the intensity of the yellow is upto 1/10th of the blue. If the intensity of yellow is less than this value then the solution will appear as blue. Using equation (3),

$$pH = pK_{In} + \log \frac{10}{1} \qquad \text{(colour of ionised form)}$$
$$= pK_{In} + 1$$

$$\text{Again } pH = pK_{In} + \log \frac{1}{10} \qquad \text{(colour of unionised form)}$$
$$= pK_{In} - 1$$

Consequently the range of indicator is $pH = pK_{In} \pm 1$ i.e., within this range of pH the indicator will appear to change from one colour to the others.

pK_{In} of some common indicators along with their colours in acidic and alkaline medium are given in the following table.

Indicator	pK_{In}	Colour in acid	Colour in alkali
(1) Phenolphthalein	8·3	Colourless	Pink
(2) Methyl orange	3·7	Red	Yellow
(3) Bromothymol blue	7·0	Yellow	Blue
(4) Thymol blue	1·51	Red	Yellow

- **Choice of Indicator :**

The choice of indicator depends upon the pH of the solution at the equivalence point. If the pH at the end-point at an acid-base titration is very close to the vicinity of $pK_{In} \pm 1$ or lie in between $pK_{In} \pm 1$ then that indicator will show a sharp colour change in that particular titration. An ideal indicator is the one whose pK_{In} *corresponds to the pH at the end point of titration.*

Examples :

Justify the use of methyl red ($pK_{In} = 5{\cdot}1$) in the titration of NH_4OH ($K_b = 1{\cdot}74 \times 10^{-5}$) with HCl solution in aqueous medium. Salt formed being decinormal.

Ans. : The range of methyl red. $pH = 5{\cdot}1 \pm 1 = 4{\cdot}1$ to $6{\cdot}1$

$K_b = 1{\cdot}74 \times 10^{-5}$

or, $pK_b = -\log(1{\cdot}74 \times 10^{-5}) = 5 - \log 1{\cdot}74 = 4{\cdot}76$.

In the titration of NH_4OH (weak base) with HCl (strong acid) the resultant pH at neutralisation point is,

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2}\log C$$
$$= 7 - 1/2 \times 4{\cdot}76 - 1/2 \log 0{\cdot}1$$
$$= 5{\cdot}12$$

Since the pH=5·12 lies between the range of methyl red (4·1−6·1), the indicator will show a sharp colour change in the above titration.

• Ostwald theory and action of indicator :

(A) Phenophthalein : Representing phenolphthalein by HP_n

$$\underset{\text{colourless}}{HPn} \rightleftharpoons H^+ + \underset{\text{pink}}{Pn^-}$$

i.e., in ionised form (Pn^-) it is coloured pink but in unionised form (HPn) it is colourless. When a few drops of NaOH is added to it, the OH^- ions furnished by NaOH react with H^+ of HPn to form practically undissociated H_2O molecule and the equilibrium is shifted towards the right. As a result, concentration of Pn^- is enhanced. Thus, the whole solution becomes pink.

Again when acid is added, the H^+ ions furnished by the acid will suppress the dissociation of HPn, the equilibrium will be shifted towards the left due to the common ion effect. As a result, the solution remains colourless. Thus, *phenolphthalein is colourless in acidic medium and pink in alkaline medium.*

• Phenolphthalein is unsuitable in the titration of weak base (NH_4OH) by strong acid (HCl)—Explain why.

This is because of the fact that NH_4OH being a very weak base furnishes so few amount of OH^- ions that it is unable to shift the equilibrium $HPn \rightleftharpoons H^+ + Pn^-$ towards right at the equivalence point. Therefore, pink colour will not appear just at the end-point. In this case *methyl red* (pK_{In}=5·1) or *methyl orange* (pK_{In}=3·7) can be profitably used.

(B) Methyl orange : It is a weak basic indicator. Representing methyl orange as MeOH.

$$\underset{\text{yellow}}{MeOH} \rightleftharpoons \underset{\text{red}}{Me^+} + OH^-$$

In acidic medium it becomes red and in alkaline medium it is yellow. H^+ ions furnished by acid combines with OH^- ions to form practically undissociated H_2O thereby shifting the equilibrium toward right increasing the concentration of Me^+ ion, which is red. Thus methyl orange appears red in acid medium. When an alkali say NaOH is added, the above equilibrium is shifted towards left due to common ion (OH^- ion) effect. Thus, methyl orange gives yellow colour in alkaline medium.

• Methyl orange is not suitable in the titration of weak acid like CH_3COOH by a strong alkali like NaOH. This is because of the fact that CH_3COOH being a weak acid furnishes so few amount of H^+ ions that they are unable to shift the equilibrium $MeOH \rightleftharpoons Me^+ + OH^-$ towards the right at the end-point. Hence red colour would not appear just at the end-point.

In this case phenolphthalein is a suitable indicator.

• The use of phenolphthalein in the titration of weak acid by a strong alkali.

pK_{In} of phenolphathalein = 8·3

Range of phenolphthalein pH = 7·3 to 9·3.

pK_a of CH_3COOH = 4·74.

pH at the end-point when 0·1(N) NaOH is titrated with 0·1(N) CH_3COOH.

$$pH = 1/2\,pK_w + 1/2\,pK_a + 1/2 \log C$$
$$= 7 + 1/2 \times 4\cdot74 + 1/2 \log 0\cdot05$$
$$= 8\cdot72$$

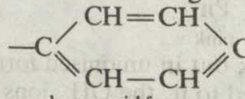
Since the value lies between the range of phenolphthalein it can be used for this titration.

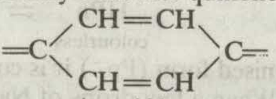
[B] **Quinonoid theory :**

This theory postulates that—

(i) All indicators are organic aromatic compounds containing at least one benzene ring.

(ii) One of the benzene rings in the indicator may exist into quinonoid form.


benzenoid form


quinonoid form

(iii) The benzenoid form is colourless or of light colour and the quinonoid form has a dark colour.

(iv) The conversion of benzenoid to quinonoid form is governed by the pH of the medium.

(v) The colour-change of the medium is due to the structural change from the benzenoid to quinonoid form at a certain specific pH of the medium.

- **Indicator to be used in the titration of Na_2CO_3 by strong acid HCl.**

Let us first consider the titration of weak carbonic acid with strong base NaOH.

$$H_2CO_3 + NaOH = NaHCO_3 + H_2O$$
$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O$$

For H_2CO_3 $K_1 = 4\cdot31 \times 10^{-7}$, $pK_1 = 6\cdot37$

Similarly $K_2 = 5\cdot61 \times 10^{-11}$, $pK_2 = 10\cdot25$

pH at the first equivalence point i.e., due to the formation of $NaHCO_3$.

$$pH_1 = \frac{1}{2}(pK_1 + pK_2) = 1/2\,(6\cdot37 + 10\cdot25) = 8\cdot31$$
$$pH_2 = 1/2\,pK_w + 1/2\,pK_2 + 1/2 \log C$$
$$= 7 + 1/2 \times 10\cdot25 + \frac{1}{2} \log 0\cdot1 = 11\cdot6 \quad [(\text{assuming } C = 0\cdot1)]$$

If *pH* is plotted against the number of moles of NaOH, two equivalence points will be obtained. One will correspond to the formation of $NaHCO_3$ and the other to the formation of Na_2CO_3. *pH* 8·31 is within the range of phenolphthalein (8·3–10·3). Hence pink colour will appear when NaOH solution is added to

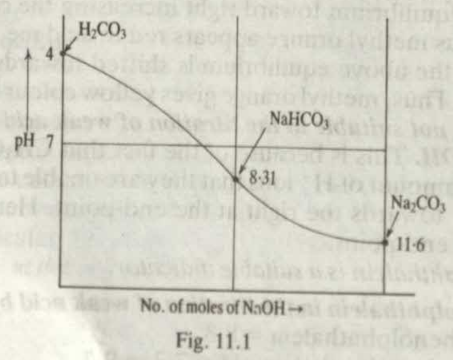


Fig. 11.1

carbonic acid solution. This indicates the first equivalence point but the pH break is not very sharp. Again since K_2 is very small, direct titration of H_2CO_3 as a dibasic acid is not possible.

Although the above titration can not be performed, the reverse process i.e., titration of Na_2CO_3 by HCl is of practical importance.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \ldots\ldots (1)$$

$$NaHCO_3 + HCl = H_2CO_3 + NaCl \ldots\ldots (2)$$

The *pH* of Na_2CO_3 is 11·6 as shown above. Equation (1) shows as Na_2CO_3 is changed to $NaHCO_3$ the *pH* changes from 11·6 to 8·31. Therefore, phenolphthalein will change colour from pink to colourless. Now if methyl orange is added to the resulting solution the colour becomes yellow. On addition of HCl from the burette the yellow colour changes and becomes orange as soon as H_2CO_3 is formed in accordance with equation (2) . (A saturated solution of H_2CO_3 has *pH* about 4·0). If, on the other hand, Na_2CO_3 is titrated in presence of methyl orange from the start 2 moles of HCl would be consumed per mole of Na_2CO_3.

$$Na_2CO_3 + 2HCl = H_2CO_3 + 2NaCl$$

In presence of phenolphthalein the number of moles of HCl would be half of this i.e., 1 mole.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

Hence it may be concluded that in presence of phenolphthalein only half of Na_2CO_3 is completely neutralised.

11·9. Solubility product.

No free molecules exist in the aqueous solution of highly soluble salt (electrolyte). But in a saturated solution of sparingly soluble salt (electrolyte) such as AgCl, $BaSO_4$ etc., a reversible reaction is set up between the solid insoluble salt and the dissociated ions, however small they might be. This results in a simultaneous equilibria among the undissolved solid, unionised dissolved solid and the free cations and anions. *This is applicable only for sparingly soluble electrolytes.*

Let us consider a saturated solution of AgCl at a constant temperature where the following equilibria exist.

$$\underset{\text{undissolved solid}}{AgCl\,(s)} \rightleftharpoons \underset{\text{saturated solution}}{AgCl} \rightleftharpoons Ag^+(aq) + Cl^-\,(aq)$$

Applying the law of mass action,

$$K = \frac{[Ag^+][Cl^-]}{\underset{(s)}{[AgCl]}} \qquad K = \text{equilibrium constant}$$

$$\text{or,}\quad K \times \underset{(s)}{[AgCl]} = [Ag^+][Cl^-]$$

In a saturated solution $[AgCl(s)]$ is constant at a fixed temperature.

$$\therefore\ K_s = [Ag^+][Cl^-]$$

K_s is called the solubility product constant for the sparingly soluble electrolyte at a constant temperature.

Similarly, (i) $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{--}$

$K_s = [Ag^+]^2[CrO_4^{--}]$

(ii) $CaF_2 \rightleftharpoons Ca^{++} + 2F^-$

$K_s = [Ca^{++}][F^-]^2$

(iii) $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{++} + 2PO_4^{---}$

$K_s = [Ca^{++}]^3[PO_4^{---}]^2$

In general, for an electrolyte, A_xB_y ionising as follows, $A_xB_y \rightleftharpoons xA^+ + yB^-$ the solubility product is given by

$$K_s = [A^+]^x [B^-]^y$$

where $[A^+]$ and $[B^-]$ are the ionic concentration of the cation and anion in a saturated solution at a fixed temperature.

- *In a saturated solution of a sparingly soluble electrolyte, the product of the ionic concentration, raised to the power equal to the stoichiometric coefficient of the species in the balanced chemical equation, is constant at a given temperature. This contant K_s is known as solubility product constant.*

- **Relation between the solubility and solubility product of a substance.** Let S be the solubility of a sparingly soluble electrolyte in moles per litre at a given temperature.

(a) *For uni-univalent electrolyte* say AgCl—

$$\underset{S\text{ moles/litre}}{AgCl} \rightleftharpoons \underset{S\text{ gram-ion/litre}}{Ag^+} + \underset{S\text{ gram-ion/litre}}{Cl^-}$$

$$K_s = [Ag^+][Cl^-] = S \times S = S^2$$

$$\text{or,}\quad S = \sqrt{K_s}$$

(b) *For bi-bivalent electrolyte* say $BaSO_4$

$$\underset{S\text{ moles/litre}}{BaSO_4} \rightleftharpoons \underset{S\text{ gram-ion/litre}}{Ba^{++}} + \underset{S\text{ gram-ion/litre}}{SO_4^{--}}$$

$$K_s = [Ba^{++}][SO_4^{--}] = S \times S = S^2$$

$$\text{or,}\quad S = \sqrt{K_s}$$

(c) *For tri-trivalent electrolyte* say $AlPO_4$

$$\underset{S\text{ moles/litre}}{AlPO_4} \rightleftharpoons \underset{S\text{ gram-ion/litre}}{Al^{+++}} + \underset{S\text{ gram-ion/litre}}{PO_4^{---}}$$

$$K_s = [Al^{+++}][PO_4^{---}] = S \times S = S^2$$

$$\text{or,}\quad S = \sqrt{K_s}$$

(d) *For uni-bivalent electrolytes* say Ag_2SO_4

$$\underset{S\text{ moles/litre}}{Ag_2SO_4} \rightleftharpoons \underset{2S\text{ gram-ion/litre}}{2Ag^+} + \underset{S\text{ gram-ion/litre}}{SO_4^{--}}$$

$$K_s = [Ag^+]^2[SO_4^{--}] = (2S)^2 \times S = 4S^3$$

$$\text{or,}\quad S = \sqrt[3]{K_s/4}$$

(e) *For bi-univalent electrolyte* say CaF_2

$$\underset{S\text{ moles/litre}}{CaF_2} \rightleftharpoons \underset{S\text{ gram-ion/litre}}{Ca^{++}} + \underset{2S\text{ gram-ion/litre}}{2F_4^-}$$

$$K_s = [Ca^{++}][F^-]^2 = S \times (2S)^2 = 4S^3$$

$$\text{or,}\quad S = \sqrt[3]{K_s/4}$$

(f) *For bi-trivalent electrolyte* say $Ba_3(PO_4)_2$

$$\underset{S\text{ moles/litre}}{Ba_3(PO_4)_2} \rightleftharpoons \underset{3S\text{ gram-ion/litre}}{3Ba^{++}} + \underset{2S\text{ gram-ion/litre}}{2PO_4^{---}}$$

$$K_s = [Ba^{++}]^3[PO_4^{---}]^2 = (3S)^3 \times (2S)^2 = 108S^5$$

$$\text{or,}\quad K_s = 108S^5 \qquad S = \sqrt[5]{\frac{K_s}{108}}$$

- **Applications of solubility product :**

The principle of solubility product controls all the precipitation as well as dissolution equilibria of sparingly soluble salts. (i) If the product of the ionic concentration in a solution is less than the K_s value, the solution is said to be unsaturated. (ii) If on the other hand, the product of the ionic concentration exceeds its K_s value, precipitation will begin till the product of the ionic concentration equals to K_s value. *Thus precipitation occurs only when the product of the ionic concentration exceeds the K_s value.*

The relation between the ionic product and the solubility product of a sparingly soluble electrolyte leads to the following generalisation—

For an electrolyte $AB \rightleftharpoons A^+ + B^-$

$$K_s = [A^+][B^-]$$

(i) A solution in which $[A^+][B^-] < K_s$, it is *unsaturated* and more solute would dissolve in it.

(ii) A solution in which $[A^+][B^-] = K_s$, it is *saturated* solution and no precipitation would occur.

(iii) If in a solution $[A^+][B^-] > K_s$, then solid AB will be precipitated i.e., if ionic product $> K_s$, precipitation would take place.

(iv) If the concentration of A^+ or B^- or both A^+ and B^- is increased by the addition of a common ion, the equilibrium would be shifted in such a direction as to decrease their concentration. In such case precipitation would occur.

(v) If either A^+ or B^- ion is removed either by complex formation or by the formation of weak electrolyte, the equilibrium will be shifted towards right, the salt is brought to solution i.e., *dissolution* of the precipitate occurs.

Examples :

Certain salts of *carbonate, phosphates, sulphides* etc., are insoluble in water but are soluble in acids. This is due to the formation of weak acids like H_2CO_3, H_3PO_4, H_2S etc. Since these acids are weak, the concentration of the anions of the above acids decreases to a value less than the value at equilibrium.

$$2H^+ + CO_3^{--} \rightleftharpoons H_2CO_3$$
$$3H^+ + PO_4^{---} \rightleftharpoons H_3PO_4$$
$$2H^+ + S^{--} \rightleftharpoons H_2S$$

So more salts go into the solution to maintain the equilibrium concentration of the anions which are removed as weak acids.

Similarly if a complexing agent is added e.g., NH_3 in $AgCl \rightleftharpoons Ag^+ + Cl^-$, the equilibrium will be shifted towards right due to the removal of Ag^+ ion from the solution as complex ion $[Ag(NH_3)_2]^+$. If excess of NH_3 is added, the whole of AgCl will go into the solution.

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

- **Common ion effect :**

Let us consider a binary weak electrolyte MA.

$$MA \rightleftharpoons M^+ + A^-$$

Applying the law of mass action,

$$K = \frac{[M^+][A^-]}{[MA]}$$

Let us suppose a strong electrolyte MB or BA, common to either cation M^+ or the anion A^- is added to the above equlibrium.

$$MB \rightleftharpoons M^+ + B^-$$
$$BA \rightleftharpoons B^+ + A^-$$

When MB is added, the M^+ ions furnished by MB will increase the concentration of M^+ ion of MA. As a result, equilibrium will be shifted towards left and more MA will be precipitated out. Same thing will happen on addition of BA which would increase the concentration of A^- ions.

Thus common ion effect is defined as the phenomenon of suppression of the degree of ionisation of a weak electrolyte by the addition of a strong electrolyte having an ion common to that furnished by the weak electrolyte.

Application of common ion effect :

(i) *Precipitation of silver chromate :* The equilibrium in a saturated solution of Ag_2CrO_4 is—

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{--}$$

Addition of a concentrated solution of $AgNO_3$ (Ag^+ ion is common) or potassium chromate (CrO_4^{--} ion is common), precipitates silver chromate by shifting the equilibrium towards left.

(ii) *Purification of common salt :* Impure sodium chloride is contaminated with $CaCl_2$ and $MgCl_2$. Pure table salt is obtained by passing dry HCl gas into a saturated solution of common salt. NaCl is ionised as Na^+ and Cl^- ions in its solution.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

When HCl gas is passed ($HCl \rightleftharpoons H^+ + Cl^-$), the Cl^- ions furnished by HCl, increases the concentration of Cl^- ions and as a result the equilibrium is shifted towards left and pure NaCl is precipitated out. Thus the addition of HCl suppresses the degree of ionisation of NaCl. $CaCl_2$ and $MgCl_2$ remain in the solution as the solution is not a saturated solution of $MgCl_2$ and $CaCl_2$. Again since the concentration of Ca^{++} and Mg^{++} in the solution of common salt is very small in comparison to that of Na^+, $[Ca^{++}]\,[Cl^-]^2 < K_s$ of $CaCl_2$ or $[Mg^{++}]\,[Cl^-]^2 < K_s$ of $MgCl_2$. As a result $CaCl_2$ or $MgCl_2$ is not precipitated.

- **Application of solubility product in qualitative analysis :**

Depending on the solubility product-value of the precipitates, the cations are divided into several groups from group-I to group-V in the analytical table for their identification. A knowledge of solubility product-values helps us in predicting the condition of precipitation.

(i) **Precipitation of Group-I :** *Precipitation of insoluble chlorides ($AgCl$, Hg_2Cl_2 and $PbCl_2$).*

To an aqueous solution of Ag^+, Hg_2^{++} or Pb^{++} ion, when dilute HCl is added, they are precipitated.

$$\begin{aligned} AgNO_3 &+ HCl = AgCl\downarrow + HNO_3 \\ Hg_2(NO_3)_2 &+ 2HCl = Hg_2Cl_2\downarrow + 2HNO_3 \\ Pb(NO_3)_2 &+ 2HCl = PbCl_2\downarrow + 2HNO_3 \end{aligned}$$

The above chlorides are sparingly soluble in water. Additions of HCl increases the concentration of Cl^- ion. Under this condition the products of their ions e.g., $[Ag^+]\,[Cl^-]$ or $[Pb^{++}]\,[Cl^-]^2$ exceed their respective solubility products and hence they are immediately precipitated out. The values of the solubility product in the table show that K_s value of Hg_2Cl_2 is the lowest, consequently it can be easily exceeded to precipitate Hg_2Cl_2. Then follows AgCl. The precipitation of AgCl and Hg_2Cl_2 becomes complete. But as the K_s of $PbCl_2$ is maximum, so even if the concentration of Cl^- is increased by adding excess of HCl, complete precipitation of $PbCl_2$ is not possible in Group-I. Some of the Pb^{++} ions are passed into subsequent group for complete precipitation.

Metallic Chloride of Gr I	Solubility product at 25°C
AgCl	$1{\cdot}5 \times 10^{-10}$
Hg_2Cl_2	$1{\cdot}2 \times 10^{-12}$
$PbCl_2$	$2{\cdot}4 \times 10^{-4}$

(ii) **Precipitation of Group-II :** Group-II contains Cu^{++}, Pb^{++}, Hg^+ and CuS are black, CdS, As_2S_3 and SnS are yellow, Sb_2S_3 is orange. Acidity of the solution is maintained around 0·3(M). H_2S is a weak acid and dissociates as $H_2S \rightleftharpoons 2H^+ + S^{--}$ in the solution. This dissociation of H_2S is suppressed by the H^+ ions produced from HCl. $HCl \rightleftharpoons H^+ + Cl^-$ (common ion effect). As a result the concentration of S^{--} ions in the solution becomes low. But this lowering of the concentration of S^{--} ion is sufficient to exceed the corresponding solubility product and to precipitate the sulphides like HgS, CuS, PbS, CdS, As_2S_3, Sb_2S_3 as the solubility products of these sulphides are very low. The sulphides like ZnS, NiS, FeS etc., have comparatively high solubility products and so they remain in the solution.

Metal sulphides of Group-II	**Solubility product at 25°C**
HgS	3×10^{-54}
PbS	4×10^{-28}
CuS	3×10^{-42}
CdS	$3{\cdot}6 \times 10^{-29}$

(iii) **Precipitation of Group-IIIA :**

Group-IIIA contains Fe^{+++}, Cr^{+++} and Al^{+++} ions. They are precipitated as $Fe(OH)_3$ (brown), $Cr(OH)_3$ (Green) and $Al(OH)_3$ (gelatinous white) when a mixture of solid NH_4Cl and NH_4OH is added to the solution containing these ions. If only NH_4OH is used instead of the mixture of NH_4Cl and NH_4OH, not only the above three ions but also the other metal ions of subsequent groups are precipitated. Though NH_4OH is a weak electrolyte, if only NH_4OH is used, the OH^- ions furnished by NH_4OH are sufficient to exceed the solubility products of not only the hydroxides of Gr.-IIIA but also that of other groups e.g., IIIB, IV and V. The solubility products of the hydroxides of Gr.-IIIA are comparatively low in comparison to the hydroxides of other metals of other subsequent groups. Now NH_4Cl being strong electrolyte dissociates completely as NH_4^+ and Cl^-. Due to the common ion effect of NH_4^+, the dissociation of NH_4OH is further decreased and consequently the concentration of OH^- ions is greatly reduced. Under this condition, the low concentration of OH^- ions is sufficient to exceed the low solubility product-values of $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$, but is not sufficient to exceed those of the hydroxides of the subsequent groups. So the hydroxides of Gr.-IIIA metals get precipitated leaving behind the other ions in the solution. Since the solubility product of $Fe(OH)_2$ is comparatively high it would not be precipitated in presence of NH_4Cl.

Metallic hydroxides		**Solubility product at 25°C**
Low solubility products—precipitated in presence of NH_4Cl	$Fe(OH)_3$	1×10^{-38}
	$Cr(OH)_3$	1×10^{-30}
	$Al(OH)_3$	1×10^{-30}
High solubility products—not precipitated in presence of NH_4Cl	$Zn(OH)_2$	1×10^{-17}
	$Fe(OH)_2$	1×10^{-15}
	$Mn(OH)_2$	1×10^{-14}
	$Ni(OH)_2$	1×10^{-14}
	$Ca(OH)_2$	1×10^{-12}
	$Mg(OH)_2$	8×10^{-6}

(iv) **Precipitation of Group-IIIB :** Gr.-IIIB contains Zn^{++}, Co^{++}, Ni^{++} and Mn^{++}. These are precipitated as sulphides from ammoniacal medium. Their solubility product-values are comparatively high. In acidic medium $[S^{--}]$ is very low hence these sulphides are not precipitated in Gr.-II with Cu, Pb, As etc. These sulphides require larger $[S^{--}]$. This condition is maintained in higher pH i.e., in ammoniacal medium.

• When H_2S is passed into a solution containing $ZnCl_2$ and $CuCl_2$ acidified with dil. HCl, only black CuS is precipitated but not ZnS—Explain why.

An aqueous solution of H_2S dissociates as—

$$H_2S \rightleftharpoons 2H^+ + S^{--}$$

Applying the law of mass action—

$$K_{H_2S} = \frac{[H^+]^2[S^{--}]}{[H_2S]}$$

$$\text{or,}\ \ [S^{--}] = \frac{K_{H_2S} \times [H_2S]}{[H^+]^2}$$

K_{H_2S} is constant at fixed temperature, $[H_2S]$ is also constant at fixed temperature.

$$\therefore\ \ [S^{--}] \propto \frac{1}{[H^+]^2}$$

i.e., increase of $[H^+]$, decreases the concentration of S^{--} ion.

$$\text{Again}\ \ K_w = [H^+][OH^-]$$

$$\text{or,}\ \ [OH^-] = K_w/[H^+]$$

K_w = ionic product of water is constant at fixed temperature.

$$\therefore\ \ [OH^-] \propto \frac{1}{[H^+]}$$

$$\therefore\ \ [S^{--}] \propto \frac{1}{[H^+]^2} \propto [OH^-]$$

i.e., the increase of $[OH^-]$, increases $[S^{--}]$

The precipitation will be completed when $[Cu^{++}]\,[S^{--}] > K_s$ of CuS and $[Zn^{++}]\,[S^{--}] > K_s$ of ZnS. As the solubility product of ZnS is enormously higher than that of CuS, low concentration of S^{--} is sufficient to exceed the smaller solubility product of CuS but not of ZnS. So for the precipitation of ZnS a higher concentration of S^{--} ion is necessary. In acid medium i.e., in higher $[H^+]$, $[S^{--}]$ becomes low and so CuS is precipitated in acid medium. In ammoniacal medium $[S^{--}]$ becomes large which is sufficient to exceed the solubility product of ZnS and hence ZnS is precipitated in ammoniacal medium but not in acid medium.

• $Mg(OH)_2$ is sparingly soluble in water but is highly soluble in NH_4Cl solution—Explain why.

$Mg(OH)_2$ in its saturated solution dissociates as follows—

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$$

$$K_s = [Mg^{++}][OH^-]^2$$

NH_4Cl is strong electrolyte, it dissociates completely into its ions. On addition of NH_4Cl to the above equilibrium NH_4^+ ion reacts with OH^- ion to form weak electrolyte NH_4OH and thus the $[OH^-]$ is considerably reduced. In order to maintain the equilibrium undisturbed, more $Mg(OH)_2$ goes into the solution and the process continues till all the $Mg(OH)_2$ are dissolved. Due to the decrease of $[OH^-]$ by NH_4Cl, the product $[Mg^{++}][OH^-]^2$ becomes less than its K_s value. Hence $Mg(OH)_2$ dissolves.

Again, NH_4Cl solution being acidic, supplies H^+ ions which react with OH^- ions to form undissociated H_2O. In order to keep the K_s value of $Mg(OH)_2$ constant, concentration of Mg^{++} ion must increase and that is posible if more of the solid $Mg(OH)_2$ goes into the solution.

11.10. Numerical problems.

1. *Find the pH of a solution of which* $[H^+] = 4 \times 10^{-4}$ *molar.*

Ans : $pH = -\log[H^+] = -\log(4 \times 10^{-4}) = 4 - \log 4$
$= 4 - 0{\cdot}602 = 3{\cdot}398.$

2. *Find the* $[H^+]$ *corresponding to* $pH = 4{\cdot}643$.

Ans : $pH = -\log[H^+]$ or, $\log[H^+] = -pH = -4{\cdot}643$
or, $\log[H^+] = -4{\cdot}643 = \overline{5}{\cdot}357$
From antilog table $0{\cdot}357 = 2{\cdot}28$.
$\therefore [H^+] = 2{\cdot}28 \times 10^{-5}$ molar.

3. *Calculate the pH of the resulting solution when 99·9 ml and 100·1 ml of (N/10) NaOH are added separately to 100 ml of (N/10) HCl.*

Ans : (i) 99·9 ml of (N/10) alkali will neutralise 99·9 ml of (N/10) HCl leaving behind 0·1 ml of (N/10) HCl unneutralised. Total volume of the solution is 199·9 ml.

$$\therefore [H^+] = \frac{0{\cdot}1 \times 0{\cdot}1}{199{\cdot}9} = 5 \times 10^{-5}$$

$$pH = -\log(5 \times 10^{-5}) = 5 - \log 5 = 4{\cdot}3010$$

(ii) When 100·1 ml of (N/10) NaOH is added to 100 ml of (N/10) HCl, there is 0·1 ml of alkali is excess. pH of the solution will be due to this 0·1 ml of alkali. Total volume is 200·1 ml.

$$\therefore [OH^-] = \frac{0{\cdot}1 \times 0{\cdot}1}{200{\cdot}1} = 4{\cdot}9 \times 10^{-5}$$

$$pOH = -\log(4{\cdot}9 \times 10^{-5}) = 5 - \log 4{\cdot}9 = 4{\cdot}3099$$

$$pH = 14 - 4{\cdot}309 = 9{\cdot}69$$

4. *Calculate the pH of 0·1(N)* CH_3COOH *solution (given* $K_a = 1{\cdot}82 \times 10^{-5}$*).*

Ans :

$$\underset{C(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{C\alpha}{H^+} + \underset{C\alpha}{CH_3COOH^-}$$

Applying Ostwald dilution law,

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} \approx C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1{\cdot}82 \times 10^{-5}}{0{\cdot}1}} = 1{\cdot}35 \times 10^{-2}$$

$$[H^+] = C\alpha = 0{\cdot}1 \times 1{\cdot}35 \times 10^{-2} = 1{\cdot}35 \times 10^{-3}$$

$$pH = -\log(1{\cdot}35 \times 10^{-3}) = 3 - \log 1{\cdot}35 = 2{\cdot}87.$$

5. *If 100 ml of 0·1(N)* CH_3COOH *be mixed with 200 ml of 0·5(N)* CH_3COONa*, what will be the pH of the resulting mixture ? Given* pK_a *of* $CH_3COOH = 4{\cdot}757$.

Ans :

$$[CH_3COOH] = \frac{0{\cdot}1 \times 100}{300}(N) = 0{\cdot}0333(N)$$

$$[CH_3COONa] = \frac{0{\cdot}5 \times 200}{300}(N) = 0{\cdot}3333(N)$$

Applying Henderson equation,

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$= 4{\cdot}757 + \log\frac{0{\cdot}3333}{0{\cdot}0333}$$

$$= 4{\cdot}757 + \log 10 = 4{\cdot}757 + 1 = 5{\cdot}757.$$

6. *A solution of* NH_4OH *is 2% ionised at 25°C in 0·1(M) concentration. Calculate the dissociation constant.*

Ans : $\alpha = \text{degree of dissociation} = \dfrac{\text{Percent dissociation}}{100} = 2/100 = 2 \times 10^{-2}$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

From Ostwald dilution law,

$$K_b = C\alpha^2 = 0\cdot1 \times (2 \times 10^{-2})^2$$

$$\text{or,}\quad K_b = 4 \times 10^{-5}$$

7. *The dissociation constant of benzoic acid is* $6\cdot6\times10^{-5}$*, calculate the pH of a solution containing 3·66 g of benzoic acid in 1500 ml of water.*

Ans : Mol. wt. of benzoic acid = 122

$$\text{No. of moles of benzoic acid} = \frac{3\cdot66}{122} = 0\cdot03$$

$$\text{Molar concentration} = \frac{0\cdot03}{1\cdot5} = 0\cdot02 \text{ mole/litre}$$

$$[H^+] = C\alpha = C\sqrt{K_a/C} = \sqrt{K_a \cdot C}$$

$$= \sqrt{6\cdot6 \times 10^{-5} \times 0\cdot02} = 11\cdot49 \times 10^{-4}$$

$$\therefore \ pH = -\log(11\cdot49 \times 10^{-4}) = 4 - \log 11\cdot49$$

$$= 4 - 1\cdot0604 = 2\cdot9396 \approx 2\cdot94.$$

8. *Calculate the degree of hydrolysis, hydrolysis constant and pH of 0·1(N)* NH_4Cl *solution. Given* K_b *for* $NH_4OH=4\times10^{-5}$ *and* $K_w=1\cdot0\times10^{-14}$

Ans : $K_h = K_w/K_b = 1\cdot0 \times 10^{-14}/4 \times 10^{-5} = 2\cdot5 \times 10^{-10}$

Let h be the degree of hydrolysis,

$$h = \sqrt{K_h/C} = \sqrt{2\cdot5\times10^{-10}/0\cdot1} = 5 \times 10^{-5}$$

$$pK_b = -\log(4 \times 10^{-5}) = 5 - \log 4 = 5 - 0\cdot6020 = 4\cdot398$$

NH_4Cl being a salt of weak base (NH_4OH) and strong acid (HCl),

$$pH = 1/2\,pK_w - 1/2\,pK_b - 1/2 \log C$$

$$= 1/2 \times 14 - 1/2 \times 4\cdot398 - 1/2 \log 0\cdot1$$

$$= 7 - 2\cdot199 + 0\cdot5$$

$$= 5\cdot301.$$

9. *Freshly precipitated* $Al(OH)_3$ *and* $Mg(OH)_2$ *are stirred vigorously in a buffer solution containing 0·25 mole/litre of* NH_4Cl *and 0·05 mole/litre of* NH_4OH*. Calculate the concentration of* Al^{+++} *and* Mg^{++} *ions in the solution. Given* K_b *of* $NH_4OH = 1\cdot8\times10^{-5}$*,* K_s *of* $Al(OH)_3=6\cdot10^{-32}$ *and* K_s *of* $Mg(OH)_2=6\times10^{-10}$ *[I.I.T. '89]*

Ans : Applying Henderson equation,

$$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log(1\cdot8 \times 10^{-5}) + \log\frac{0\cdot25}{0\cdot05}$$

$$= 5 - \log 1\cdot8 + \log 5$$

$$= 5 - 0\cdot2552 + 0\cdot6989$$

$$= 5\cdot4437$$

$$\text{or,} -\log[OH^-] = 5\cdot4437$$

$$\text{or,}\ [OH^-] = 3\cdot599 \times 10^{-6} \text{ mole/litre.}$$

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$$

$$K_s = [Mg^{++}][OH^-]^2$$

$$\text{or,}\ [Mg^{++}] = K_s/[OH^-]^2 = \frac{6 \times 10^{-10}}{(3\cdot599 \times 10^{-6})^2} = 0\cdot4632 \times 10^2$$

$$\text{or,}\ [Mg^{++}] = 46\cdot32 \text{ moles/litre}$$

$$\text{Similarly,}\ [Al^{+++}] = \frac{K_s}{[OH^-]^3} = \frac{6 \times 10^{-32}}{(3\cdot599 \times 10^{-6})^3}$$

$$= 1\cdot286 \times 10^{-15} \text{ mole/litre.}$$

10. *You are titrating 100 ml of 0·1(N) CH_3COOH with 0·1(N) NaOH from a burette. Calculate the pH of the resulting solution when (a) 0 ml, (b) 90 ml, (c) 100 ml, (d) 101 ml of NaOH is added. (Given $K_a = 1{\cdot}82 \times 10^{-5}$).*

Ans : (a) CH_3COOH is a weak acid,
Applying Ostwald dilution law,

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1{\cdot}82 \times 10^{-5}}{0{\cdot}1}} = 1{\cdot}35 \times 10^{-2}$$

$$[H^+] = C\alpha = 0{\cdot}1 \times 1{\cdot}35 \times 10^{-2} = 1{\cdot}35 \times 10^{-3}$$

$$pH = -\log(1{\cdot}35 \times 10^{-3}) = 3 - \log 1{\cdot}35 = 2{\cdot}87$$

(b) 90 ml of 0·1(N) alkali will neutralise 90 ml of 0·1(N) CH_3COOH to form 90 ml of CH_3COONa. The resulting solution now contains 10 ml of CH_3COOH and 90 ml of CH_3COONa and acts as a buffer.

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \quad \text{Now}\, pK_a = -\log(1{\cdot}82 \times 10^{-5}) = 5 - 0{\cdot}26 = 4{\cdot}74$$

$$= 4{\cdot}74 + \log\frac{\frac{90 \times 0{\cdot}1}{190}}{\frac{10 \times 0{\cdot}1}{190}}$$

$$= 4{\cdot}74 + \log 9 = 4{\cdot}74 + 0{\cdot}9542$$

$$= 5{\cdot}69.$$

(c) 100 ml of alkali will neutralise 100 ml of CH_3COOH to form 200 ml of CH_3COONa, a salt of strong base and weak acid.

$$pH = 1/2\, pK_w + 1/2\, pK_a + 1/2 \log C$$

$$= 7 + 2{\cdot}37 + 1/2 \log 0{\cdot}05$$

$$= 8{\cdot}719$$

(d) On adding 101 ml of NaOH, 100 ml of CH_3COOH will form CH_3COONa and 1 ml of 0·1(N) NaOH will remain as excess. In presence of strong alkali (NaOH) the pH of the resulting solution will be due to 1 ml of 0·1(N) NaOH.

$$[OH^-] = \frac{1 \times 0{\cdot}1}{201} = \frac{1}{2010}$$

$$pOH = -\log\frac{1}{2010} = 3{\cdot}3032$$

$$pH = 14 - 3{\cdot}3032 = 10{\cdot}6968.$$

11. *Calculate the pH at which $Fe(OH)_3$ gets precipitated if $[Fe^{+++}] = 10^{-2}(M)$ and K_s for $Fe(OH)_3 = 3{\cdot}8 \times 10^{-38}$.*

Ans : $[Fe^{+++}][OH^-]^3 = 3{\cdot}8 \times 10^{-38}$

$$\text{or, } [OH^-] = \left(\frac{3{\cdot}8 \times 10^{-38}}{10^{-2}}\right)^{1/3} = 1{\cdot}561 \times 10^{-12}$$

$$\text{or, } -\log[OH^-] = -1/3(\log 3{\cdot}8 + \log 10^{-38} - \log 10^{-2}) = -1/3(0{\cdot}5797 - 38 + 2)$$

$$\text{or, } pOH = 11{\cdot}81$$

$$\text{or, } pH = 14 - 11{\cdot}81 = 2{\cdot}19.$$

12. *Calculate the solubility product of PbI_2 if the solubility of PbI_2 is 0·7 gram per litre.*

Ans : Mol. wt. of $PbI_2 = 461$

$$\text{Solubility of } PbI_2 = \frac{0{\cdot}7}{461} = 0{\cdot}00152 \text{ mole/litre.}$$

$$\begin{array}{cccc} PbI_2 & \rightleftharpoons & Pb^{++} & + \quad 2I^- \\ 0{\cdot}00152 \text{ mole/litre} & & 0{\cdot}00152 \text{ mole/litre} & 2 \times 0{\cdot}00152 \text{ mole/litre} \end{array}$$

$$K_s = [Pb^{++}][I^-]^2 = (1{\cdot}52 \times 10^{-3})(2 \times 1{\cdot}52 \times 10^{-3})^2 = 1{\cdot}4 \times 10^{-8}$$

13. *The solubility product of $Pb_3(PO_4)_2$ is $1{\cdot}5\times10^{-22}$. Calculate the solubility of the salt in gram/litre.*

Ans :
$$\underset{S}{Pb_3(PO_4)_2} \rightleftharpoons \underset{3S}{3Pb^{++}} + \underset{2S}{2PO_4^{---}}$$

Let the solubility of $Pb_3(PO_4)_2$ be S mole per litre.

$$K_s = [3S]^3\,[2S]^2 = 108S^5$$
$$\text{or,}\quad 108S^5 = 1{\cdot}5\times10^{-22}$$
$$\text{or,}\quad S = 1{\cdot}7\times10^{-7}\ \text{mole/litre.}$$

Mol. wt. of $Pb_3(PO_4)_2 = 811{\cdot}6$

$$\text{Solubility} = 1{\cdot}7\times10^{-7}\times811{\cdot}6 = 13{\cdot}79\times10^{-5}\ \text{gram/litre.}$$

14. *Which one is more soluble between $CuCO_3$ ($K_s=2{\cdot}5\times10^{-10}$) and Ag_2CO_3 ($K_s=8{\cdot}2\times10^{-12}$) ?*

Ans :
$$\underset{S\ \text{mole/litre}}{CuCO_3} \rightleftharpoons \underset{S\ \text{mole/litre}}{Cu^{++}} + \underset{S\ \text{mole/litre}}{CO_3^{--}}$$
$$K_s = [Cu^{++}]\,[CO_3^{--}] = S\times S = S^2$$
$$\text{or,}\quad S = \sqrt{K_s} = (2{\cdot}5\times10^{-10})^{1/2} = 1{\cdot}6\times10^{-5}\ \text{mole/litre}$$
$$\underset{S}{Ag_2CO_3} \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{CO_3^{--}}$$
$$K_s = [Ag^+]^2\,[CO_3^{--}] = (2S)^2\cdot(S) = 4S^3$$
$$\text{or,}\quad S = \left(\frac{K_s}{4}\right)^{\frac{1}{3}} = \left(\frac{8{\cdot}2\times10^{-12}}{4}\right)^{\frac{1}{3}} = 1{\cdot}27\times10^{-4}\ \text{mole/litre.}$$

Thus, it is proved that Ag_2CO_3 is more soluble than $CuCO_3$.

15. *At 25°C the solubility of Ag_2SO_4 is 0·026 gram-mole/litre. Calculate its solubility product at this temperature.* [*W.B.J.E. '86*]

Ans :
$$\underset{S}{Ag_2SO_4} \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{SO_4^{--}}$$
$$K_s = [Ag^+]^2\,[SO_4^{--}] = (2S)^2\,(S) = 4S^3.$$
$$S = 0{\cdot}026\ \text{mole/litre}$$
$$K_s = 4\times(0{\cdot}026)^3 = 7{\cdot}03\times10^{-5}$$

16. *The solubility product of CaF_2 is $3{\cdot}9\times10^{-11}$ at 298K what is the solubility of the above salt in 1 litre of 0·1(N) NaF solution ?* [*A.I.H.S. '89*]

Ans : Let S mole/litre be the new solubility of CaF_2 in 0·1(N) NaF medium.

$$\underset{S}{CaF_2} \rightleftharpoons \underset{S}{Ca^{++}} + \underset{2S}{2F^-}$$
$$\underset{0\cdot1}{NaF} \rightleftharpoons \underset{0\cdot1}{Na^+} + \underset{0\cdot1}{F^-}$$

$[Ca^{++}] = S$ gram-ion/litre, $[F^-] = (0{\cdot}1 + 2S)$ gram-ion/litre.

$$K_s = [Ca^{++}]\,[F^-]^2 = S\times(0{\cdot}1+2S)^2 = S\,(0{\cdot}01 + 0{\cdot}4S + 4S^2)$$
$$= 0{\cdot}01S + 0{\cdot}4S^2 + 4S^3$$

Since S is small, the higher powers of S is neglected.

$$\therefore\ 0{\cdot}01S = 3{\cdot}9\times10^{-11}$$
$$\text{or,}\quad S = \frac{3{\cdot}9\times10^{-11}}{0{\cdot}01} = 3{\cdot}9\times10^{-9}\ \text{gram-mole/litre}$$

Mol. wt. of $CaF_2 = 78$

$$\therefore\ S = 3{\cdot}9\times10^{-9}\times78 = 3{\cdot}04\times10^{-7}\ \text{g/lit}$$

17. *How many moles of calcium hydroxide must be dissolved to produce 250 ml of an aqueous solution of pH 10·65 ? Assume complete dissociation.* [*Roorke '87*]

Ans. : We know, $pH + pOH = 14$

$$\therefore\ pOH = 14 - pH = 14 - 10{\cdot}65 = 3{\cdot}35$$
$$\therefore\ \log[OH^-] = -3{\cdot}35$$

or, $[OH^-] = 4{\cdot}47 \times 10^{-4}$ mole/litre

No. of moles of OH^- in 250 ml = $\dfrac{4{\cdot}47 \times 10^{-4}}{4} = 1{\cdot}12 \times 10^{-4}$

As $2OH^-$ ions are present in 1 mole of $Ca(OH)_2$

$\therefore$ No. of moles of $Ca(OH)_2 = \dfrac{1{\cdot}12 \times 10^{-4}}{2} = 0{\cdot}56 \times 10^{-4}$.

18. *The dissociation constant of a weak acid HA is $4{\cdot}9 \times 10^{-8}$. After making the necessary approximations, calculate (i) percentage ionisation, (ii) pH and (iii) OH^- concentration in a decimolar solution of the acid.* [*I.I.T. '83*]

Ans.(i) $HA \rightleftharpoons H^+ + A^-$

Let α is the degree of ionisation of HA (decimolar acid).

So $[H^+] = 0{\cdot}1\alpha$, $[A^-] = 0{\cdot}1\alpha$ and $[HA] = 0{\cdot}1(1-\alpha)$

$\therefore K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{0{\cdot}1\alpha \times 0{\cdot}1\alpha}{0{\cdot}1(1-\alpha)} = \dfrac{0{\cdot}1\alpha^2}{1-\alpha}$

Since HA is weak, $(1-\alpha) \approx 1$

$\therefore K_a = \dfrac{0{\cdot}1\alpha^2}{1}$

or, $4{\cdot}9 \times 10^{-8} = 0{\cdot}1\alpha^2$ or, $\alpha = \sqrt{\dfrac{4{\cdot}9 \times 10^{-8}}{0{\cdot}1}}$ or, $\alpha = 7 \times 10^{-4}$

Percentage ionisation = $100 \times 7 \times 10^{-4} = 7 \times 10^{-2}$ %.

(ii) $[H^+] = 0{\cdot}1\alpha = 0{\cdot}1 \times 7 \times 10^{-4}$ mole/litre
$= 7 \times 10^{-5}$ mole/litre.

Now $pH = -\log[H^+] = -\log(7 \times 10^{-5})$
$= 5 - \log 7 = 5 - 0{\cdot}8451$
$= 4{\cdot}1549$.

(iii) $[H^+] = 7 \times 10^{-5}$ mole/litre
$K_w = [H^+] \times [OH^-]$
or, $1 \times 10^{-14} = 7 \times 10^{-5} \times [OH^-]$
or, $[OH^-] = \dfrac{1 \times 10^{-14}}{7 \times 10^{-5}} = 1{\cdot}43 \times 10^{-10}$ mole/litre.

19. *What is the pH of 1(M) solution of acetic acid ? To what volume must one litre of this solution be diluted, so that the pH of the resulting solution will be twice that of the original value ? $K_a = 1{\cdot}8 \times 10^{-5}$.* [*I.I.T. '90*]

Ans. Acetic acid is a weak acid.

So, degree of ionisation of the acid $\alpha = \sqrt{K_a \times V}$. Here $V = 1$ litre.

$\therefore \alpha = \sqrt{1{\cdot}8 \times 10^{-5} \times 1} = 4{\cdot}24 \times 10^{-3}$
$[H^+] = \alpha \times C = 4{\cdot}24 \times 10^{-3} \times 1 = 4{\cdot}24 \times 10^{-3}$
$\log[H^+] = \log(4{\cdot}24 \times 10^{-3})$
or, $-\log[H^+] = -\log(4{\cdot}24 \times 10^{-3})$
or, $pH = -\log 4{\cdot}24 - \log 10^{-3}$
or, $pH = 3 - 0{\cdot}6274 = 2{\cdot}3726$.

Let the volume of the new solution = V

$\therefore$ the molarity of the new solution = $1/V$

$[H^+] = \sqrt{K_a \times C}$ As $C = 1/V$

$= \sqrt{\dfrac{K_a \times 1}{V}} = \sqrt{\dfrac{1{\cdot}8 \times 10^{-5}}{V}}$

$[H^+] = \dfrac{4{\cdot}2 \times 10^{-3}}{\sqrt{V}}$

Taking log on both sides,

$\log[H^+] = \log \dfrac{4{\cdot}2 \times 10^{-3}}{\sqrt{V}}$

or, $-\log[H^+] = -\log \dfrac{4{\cdot}2 \times 10^{-3}}{\sqrt{V}}$

$$\text{or,}\qquad \text{pH} = -\log \frac{4\cdot2\times10^{-3}}{\sqrt{V}}$$

Given that pH of new solution is twice that of the original.

$$\therefore\ -\log \frac{4\cdot24\times10^{-3}}{\sqrt{V}} = -2\log 4\cdot24\times10^{-3}$$

$$\text{or, } \log \frac{4\cdot24\times10^{-3}}{\sqrt{V}} = \log\,(4\cdot24\times10^{-3})^2$$

$$\text{or, } \frac{4\cdot24\times10^{-3}}{\sqrt{V}} = (4\cdot24\times10^{-3})^2$$

$$\text{or, } \sqrt{V} = \frac{4\cdot24\times10^{-3}}{(4\cdot24\times10^{-3})^2} = \frac{1}{4\cdot24\times10^{-3}}$$

$$\text{or, } V = \left(\frac{1}{4\cdot24\times10^{-3}}\right)^2 = 55\cdot6\times10^3\ \text{litre.}$$

20. *Calcium lactate is a salt of a weak organic acid and is represented as Ca(Lac)$_2$. A saturated solution of Ca(Lac)$_2$ contains 0·13 mole of this salt in 0·5 litre solution. The pOH of this solution is 5·6. Assuming complete dissociation of the salt, calculate* K_a of lactic acid. *[Roorke '91]*

Ans.

$$\begin{array}{cccc} \text{Ca(Lac)}_2 & \rightleftharpoons \ \text{Ca}^{++} & + & 2\,\text{Lac}^- \\ 0\cdot13/0\cdot5 & & & 2\times0\cdot26=0\cdot52 \\ =0\cdot26\ \text{mole/litre} & & & \text{mole/litre} \end{array}$$

∴ Concentration of lactate ion C = 0·52(M)

Now, pOH=5·6 ∴ pH=14−5·6=8·4

$K_w = 10^{-14}$ or, $\log K_w = -14$.

For a salt of weak acid and strong alkali we get,

$$\text{pH} = 1/2\,pK_w + 1/2\,pK_a + 1/2\log \text{C}$$

$$\text{or, } 8\cdot4 = 7 + 1/2\,pK_a + 1/2\times\log 0\cdot52$$

$$\text{or, } 8\cdot4 = 7 + 1/2\,pK_a - 0\cdot142$$

$$\text{or, } 1/2\,pK_a = 8\cdot4 - 6\cdot858 = 1\cdot542$$

$$\text{or, } pK_a = 1\cdot542\times2 = 3\cdot084$$

$$\text{or, } -\log K_a = 3\cdot084$$

$$\text{or, } \log K_a = -3\cdot084$$

$$\text{or, } \log K_a = \bar{4}\cdot916$$

$$\text{or, } K_a = 8\cdot26\times10^{-4}$$

21. *How may gram-mole of HCl will be required to prepare 1 litre of a buffer solution (containing NaCN and HCN) of pH 8·5, using 0·01 gram formula weight of NaCN ? K dissociation (HCN)=4×10^{-10}.* *[I.I.T. '88]*

Ans. We know that, $\text{pH} = pK_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$

Let *x* moles of HCl are added to NaCN. Now *x* mole of HCl will react with NaCN to produce *x* mole of HCN.

$$\begin{array}{lccccc} & \text{HCl} & + \ \text{NaCN} & \rightarrow & \text{NaCl} & + \ \text{HCN} \\ \text{At equilibrium} & x & (0\cdot01-x) & & & x \end{array}$$

For an acidic buffer, $\text{pH} = -\log K_a + \log \dfrac{[\textit{salt}]}{[\text{acid}]}$

$$\text{or, } 8\cdot5 = -\log\,(4\cdot1\times10^{-10}) + \log\left(\frac{0\cdot01-x}{x}\right)$$

$$\text{or, } 8\cdot5 = 10 - \log 4\cdot1 + \log\left(\frac{0\cdot01-x}{x}\right)$$

$$\text{or, } 8\cdot5 = 10 - 0\cdot613 + \log\left(\frac{0\cdot01-x}{x}\right)$$

$$\text{or, } \log\left(\frac{0{\cdot}01-x}{x}\right) = -0{\cdot}887$$

$$\text{or, } \log\left(\frac{0{\cdot}01-x}{x}\right) = \log 0{\cdot}1296$$

$$\text{or, } \frac{0{\cdot}01-x}{x} = 0{\cdot}1296 \quad \text{or, } x = 8{\cdot}85 \times 10^{-3}\text{M.}$$

22. *A 40·0 ml solution of a weak base, BOH is titrated with 0·1(N) HCl solution. The pH of the solution is found to be 10·04 and 9·14 after adding of 5 ml and 20 ml of the acid respectively. Find out the dissociation constant of the base.* [*I.I.T. '91*]

Ans. : Let x mole per litre be the concentration of the base BOH and K_b its dissociation constant.

For basic buffer—

$$\text{pH} = 14 - pK_b - \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Not for adding 5 ml of 0·1 HCl pH becomes 10·04.

$$\therefore\ 10{\cdot}04 = 14 - pK_b - \log \frac{5 \times 0{\cdot}1 \times 1000}{40 \times x \times 1000 - 5 \times 0{\cdot}1 \times 1000}$$

$$\text{or, } 10{\cdot}04 = 14 - pK_b - \log \frac{0{\cdot}5}{40x - 0{\cdot}5} \ \ldots\ldots(1)$$

For adding 20 ml of 0·1N HCl, the pH becomes 9·14.

$$\therefore\ 9{\cdot}14 = 14 - pK_b - \log \frac{20 \times 0{\cdot}1 \times 10^{-3}}{40x \times 10^{-3} - 20 \times 0{\cdot}1 \times 10^{-3}}$$

$$\text{or, } 9{\cdot}14 = 14 - pK_b - \log \frac{2}{40x - 2} \ \ldots\ldots(2)$$

Subtracting (2) from (1) weight,

$$0{\cdot}9 = \log \frac{2}{40x-2} - \log \frac{0{\cdot}5}{40x - 0{\cdot}5}$$

$$\text{or, } 0{\cdot}9 = \log\left(\frac{2}{40x-2} \times \frac{40x-0{\cdot}5}{0{\cdot}5}\right)$$

$$\text{or, } \log 7{\cdot}943 = \log \frac{2\,(40x - 0{\cdot}5)}{0{\cdot}5\,(40x-2)}$$

or, $x = 0{\cdot}088$ mole/litre.

Putting the value of x in (1) we get $10{\cdot}04 = 14 - pK_b - \log \dfrac{0{\cdot}5}{40 \times 0{\cdot}088 - 0{\cdot}5}$

Solving $K_b = 1{\cdot}828 \times 10^{-5}$

23. *Concentration of HCN and NaCN in a solution is 0·01(M) each. Calculate the concentration of* H^+ *and* OH^- *ions if the dissociation constant of HCN is* $7{\cdot}2 \times 10^{-10}$ [*Roorke Eng. '91*]

Ans. :

$$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$$

$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} \ \ldots\ldots\text{(i) and } K_w = [\text{H}^+][\text{OH}^-] \ldots\ldots\text{(ii)}$$

Dividing (ii) by (i) weight, $\quad K_w/K_a = \dfrac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]}$

As NaCN is completely ionised $[\text{CN}^-] = 0{\cdot}01(\text{M})$ and $[\text{HCN}] = 0{\cdot}01(\text{M})$

$$\therefore\ K_w/K_a = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]} = \frac{[\text{OH}^-] \times 0{\cdot}01}{0{\cdot}01} = [\text{OH}]$$

$\therefore$ Now, $K_w = 10^{-14}$ and $K_a = 7{\cdot}2 \times 10^{-10}$

$$\therefore\ [\text{OH}^-] = \frac{10^{-14}}{7{\cdot}2 \times 10^{-10}} = \frac{10}{7{\cdot}2} \times 10^{-5} = 1{\cdot}39 \times 10^{-5}\ \text{mole/litre.}$$

$$[\text{H}^+] = K_w/[\text{OH}^-] = \frac{10^{-14}}{1{\cdot}39 \times 10^{-5}} = 7{\cdot}2 \times 10^{-10}$$

or, $[\text{H}^+] = 7{\cdot}2 \times 10^{-10}$ mole/litre.

24. *The solubility product of $Ca(OH)_2$ at 25°C is $4\cdot42\times10^{-5}$. A 500 ml of saturated solution of $Ca(OH)_2$ is mixed with equal volume of $0\cdot4(M)$ NaOH. How much $Ca(OH)_2$ in mg is precipitated ?* [*I.I.T. '92*]

Ans. : Let S be the solubility of $Ca(OH)_2$ in mole/litre.

$$S = \sqrt[3]{K_s/4} = \sqrt[3]{4\cdot42\times10^{-5}/4} = 0\cdot0223 \text{ mole/litre.}$$

Amount of Ca^{++} in 500 ml solution $= \dfrac{0\cdot223\times500}{1000} = 0\cdot01115$ mole/litre. When 500 ml of $Ca(OH)_2$ is mixed with equal volume of $0.4(M)$ NaOH, the volume becomes double, hence $[OH^-] = 0\cdot2M$.

We know, $Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$

$$[Ca^{++}] = \frac{K_{sp}}{[OH]^2} = \frac{4\cdot42\times10^{-5}}{(0\cdot2)^2} = 0\cdot001105M$$

$Ca(OH)_2$ precipitated $= 0\cdot01115 - 0\cdot001105 = 0\cdot010045M$

Weight of $Ca(OH)_2$ precipitate $= 0\cdot010045\times74$ [Mol. wt. of $Ca(OH)_2 = 74$]

$= 0\cdot7433$ g $= 743\cdot3$ mg.

25. *The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentration. What volume of $5(M)$ $NaHCO_3$ solution should be mixed with a 10 ml sample of blood which is $2(M)$ in H_2CO_3 in order to maintain a pH of 7·4 ? K_a for H_2CO_3 in blood is $7\cdot8\times10^{-7}$.* [*I.I.T. 1993*]

Ans. : K_a for H_2CO_3 is $7\cdot8\times10^{-7}$; $pK_a = -\log 7\cdot8\times10^{-7} = 6\cdot108$

Applying Henderson's equation,

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$7\cdot4 = 6\cdot108 + \log\frac{5\times V}{4\times10} \text{ (since 2M = 4N)}$$

$$\text{or, } \log V - \log 8 = 1\cdot292$$

$$\log V = 2\cdot1951$$

$$V = 156\cdot7 \text{ ml.}$$

26. *How will the degree of dissociation of a $0\cdot1$ (M) solution of acetic acid change if 8·2 g of anhydrous sodium acetate are added to 1 litre of the solution ? (K_a of acetic acid is $1\cdot8\times10^{-5}$)* [*Joint Ent. '93*]

Ans. : We know $K_a = \dfrac{C\alpha\times C\alpha}{C(1-\alpha)} = \dfrac{C\alpha^2}{(1-\alpha)}$ where C=concentration and α=degree of dissociation

Here, for 0·1 M solution $1\cdot8\times10^{-5} = \dfrac{0\cdot1\alpha^2}{1-\alpha}$

Since $1-\alpha\approx$ we get $1\cdot8\times10^{-5} = 0\cdot1\alpha^2$

$$\text{or, } \alpha^2 = 1\cdot8\times10^{-4}$$

$$\text{or, } \alpha = \sqrt{1\cdot8\times10^{-4}}$$

$$= 1\cdot34\times10^{-2}$$

Concentration of sodium acetate solution $= 8\cdot2/82 = 0\cdot1$ M

Let α_1 be the degree of dissociation in presence of the salt.

$$\therefore\ K_a = \frac{0\cdot1\alpha_1(0\cdot1\alpha_1+0\cdot1)}{0\cdot1(1-\alpha_1)} = \frac{0\cdot1\alpha_1(1+\alpha_1)}{(1-\alpha_1)}$$

Since $(1+\alpha_1)\approx1$ and $(1-\alpha_1)\approx1$

We get, $K_a = 0\cdot1\alpha_1$

$$\text{or, } 1\cdot8\times10^{-5} = 0\cdot1\alpha_1$$

$$\text{or, } \alpha_1 = 1\cdot8\times10^{-4}$$

• Exercise •

1. State Ostwald dilution law and give the expression for Ostwald dilution law. How far is it applicable in practice ? State the significance of dissociation constant. [*I.S.C. '86*]

2. Distinguish between—(a) strong electrolyte and (b) weak electrolyte.

3. Prove that the ionisation constant and ionic product of water is not same.

4. Define pH and pOH. Show that pH + pOH = 14.
Show that while the pH of 0·1(M) HCl is 1 that of 0·1(M) CH_3COOH is not 1.

5. Define—(a) degree of ionisation, (b) hydrolysis constant, (c) common ion effect, (d) hydrolysis.

6. What do you mean by hydrolysis of salt. Explain with suitable illustration. [*W.B.J.E.* '*81*, '*83*]

7. Explain why—

(i) An aqueous solution of NH_4Cl is acidic. [*W.B.J.E. '84*]

(ii) When Na_2CO_3 solution is added to $FeCl_3$ solution ferric carbonate is not precipitated. [*I.I.T. '81*]

(iii) An aqueous solution of ammonium formate is feebly acidic. [*H.S.(T) '87*]

(iv) An aqueous solution of NaCl is neutral but that of NH_4Cl is acidic. [*W.B.J.E. '82*]

(v) An aqueous solution of $FeCl_3$ is acidic but that of Na_2CO_3 is alkaline. [*H.S. '84*]

(vi) An aqueous solution of $CuSO_4$ is acidic. [*W.B.J.E. '89*]

(vii) A brown precipitate results when $NaHCO_3$ is added to an aqueous solution of $FeCl_3$. [*H.S.(T) '83*]

8. Distinguish between hydrolysis and neutralisation.

9. Derive a relation between the hydrolysis constant and dissociation constant of a salt of strong acid and weak base. [*Maharashtra Board '86*]

10. What is buffer solution ? Explain the mechanism of buffer action. [*A.I.H.S. '88*]

11. What is an indicator. What do you mean by range of indicator ? [*W.B.J.E. '93*]

12. Discuss Ostwald theory of indicator. Show that pH = $pK_{In} \pm 1$.

13. What indicator would you use in the titration of (a) strong acid and strong base, (b) strong acid and weak base, (c) weak acid and strong base.

14. Explain why—

(a) A sharp end point is not obtained when NH_4OH is titrated with CH_3COOH, (b) Methyl orange is not a suitable indicator for oxalic acid and NaOH titration [*A.I.H.S. '87*] (c) The colour of a solution of NH_3 containing phenolphthalein falls and eventually disappear when NH_4Cl is gradually added to it, (d) In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of acid required at the equivalence point is twice that of the acid required using phenolphthalein as the indicator. [*I.I.T. '91*], (e) Phenolphthalein is colourless in acidic but pink in alkaline medium. [*H.S.(T) '87*]

15. Explain the term solubility product.

16. What is the effect of common ion in the solubility of a sparingly soluble salt. How is pure NaCl prepared from common salt ?

17. Discuss the analytical importance of solubility product. If *S* be the solubility of $Ca_3(PO_4)_2$ in moles per litre, what would be its solubility product ?

18. Explain why—(a) When H_2S is passed into acidified $ZnSO_4$ solution, there would be no white precipitate of ZnS. [*H.S.(T) '83*]

(b) Pure NaCl is precipitated when HCl gas is passed into a saturated solution of brine.

(c) $Mg(OH)_2$ is sparingly soluble in water but highly soluble in NH_4Cl solution. [*I.S.C. '70*]

(d) When H_2S is passed into a mixture of $CuCl_2$ and $ZnCl_2$ solution acidified with dil. HCl only Cus precipitates but not ZnS.

(e) $Ba_3(PO_4)_2$ is sparingly soluble in water but highly soluble in dilute HCl.

(f) A mixture of NH_4Cl and NH_4OH is used in the precipitation of metallic hydroxides of Gr.-IIIA.

(g) AgCl is sparingly soluble in water but highly soluble in NH_3.

(h) When NH_4Cl and NH_4OH are added to a mixture of solution containing both Al^{+++} precipitated only, but when NaCl and NaOH are added both the hydroxides are simultaneously precipitated.

(i) The aqueous solution of $NaHSO_4$ is acidic but the aqueous solution of $NaHCO_3$ is alkaline.

(j) The pH of an aqueous solution of sodium acetate is more than 7.

(k) The pH of a buffer solution does not change on the addition of a small amount of acid or alkali.

(l) Common salt is used for salting out soap.

19. Explain the term common ion effect. How is it useful in the qualitative analysis ? [*Maharashtra Board '85*]

20. Amongst the various alternatives given below each sub question, choose the correst answer—

(i) Which of the following salt solution is basic ?
(a) HOCl, (b) NaOCl, (c) $NaHSO_4$, (d) NH_4NO_3 [***Ans.*** (b)]

(ii) The pH of 10^{-8} molar solution of HCl is
(a) 8, (b) – 8, (c) between 7-8, (d) between 6-7. [***Ans.*** (d)] *[I.I.T. '81]*

(iii) An acidic buffer solution can be prepared by mixing the solution of
(a) $CH_3COONa + CH_3COOH$, (b) $NH_4Cl + NH_4OH$, (c) $H_2SO_4 + Na_2SO_4$, (d) NaCl + NaOH.
[***Ans.*** (a)] *[I.I.T. ' 81]*

(iv) A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of the buffer is
(a) 4, (b) 7, (c) 10, (d) 14. [***Ans.*** (a)] *[I.I.T. '84]*

(v) At 90°C, pure water has $[H_3O]^+ = 10^{-6}$ mole lit^{-1}. The value of K_w at 90°C is
(a) 10^{-6}, (b) 10^{-8}, (c) 10^{-12}, (d) 10^{-14}. [***Ans.*** (c)] *[MLNR '90]*

(vi) The compound whose 0·1 M solution basic is
(a) CH_3COONH_4, (b) NH_4Cl, (c) $(NH_4)_2SO_4$, (d) CH_3COONa. [***Ans.*** (d)] *[I.I.T. '86]*

(vii) A weak acid has $\alpha = 1 \times 10^{-4}$, the K for its reaction with a strong base is
(a) 1×10^{-4}, (b) 1×10^{-10}, (c) 1×10^{10}, (d) 1×10^{14}. [***Ans.*** (b)] *[I.I.T. '84]*

(viii) The pK_a of aspirin is 3·5. The pH of gastic juice in human stomach is 2—3 and the pH in small intestine is about 8. Aspirin will be
(a) unionised in the small intestine and in the stomach (b) completely ionised in small intestine and in the stomach (c) ionised in the stomach and almost unionised in the small intestine (d) ionised in the small intestine and almost unionised in the stomach. [***Ans.*** (c)] *[I.I.T. '88]*

- **Numerical problems :**

1. Calculate the pH of the following solutions at 298K assuming complete ionisation (i) a solution containing 2 g of NaOH in 800 ml of water, (ii) A solution of $3{\cdot}1\times10^{-3}$(M) HNO_3.
[***Ans.*** (i) = 12·8, (ii) = 2·5]

2. At 298K the degree of dissociation of a weak monobasic acid in $6{\cdot}6\times10^{-2}$(M) solution is 0·0145. Calculate the degree of dissociation of 0·02(M) solution of the acid at the same temperature.
[***Ans.*** $2{\cdot}64 \times 10^{-2}$]

3. A 0·01(M) solution of NH_4OH is 4·5% ionised. Calculate the concentration of OH^- ions.
[***Ans.*** $4{\cdot}5 \times 10^{-4}$]

4. A 0·01(M) solution of an acid dissociates to the extent 10%. What is dissociation constant ?
[***Ans.*** $1{\cdot}11 \times 10^{-4}$]

5. When 0·001 mole of an acid is added to 250 ml of a buffer solution, pH decreases by 0·01 unit. Calculate the buffer capacity of the system.
[***Ans.*** 0·4]

$$\left[\textbf{Hints :}\ \text{Buffer capacity} = \frac{\text{No. of moles of acid or base added per litre}}{\text{Change of pH}}\right]$$

6. A solution of a salt of NH_4OH and HCl has pH=5. If the hydrolysis constant be 1×10^{-9}, find the concentration of the salt.
[***Ans.*** 0·1(M)]

7. Calculate the hydrolysis constant of NH_4CN if $K_{HCN}=7{\cdot}2\times10^{-10}$ and $K_{NH_4OH}=1{\cdot}75\times10^{-10}$.
[***Ans.*** $K_h=7{\cdot}9\times10^{-1}$]

8. Calculate the (i) degree of hydrolysis, (ii) pH of 0.1 (M) solution of NH_4Cl at 298 K.
[***Ans.*** $K_h=5{\cdot}6\times10^{-10}$, pH=5·13]

9. Calculate $[H^+]$ of 0·1 (M) H_2S solution.
[***Ans.*** 1×10^{-4} M]

10. A solution is prepared by mixing 100 ml of 0·01 (M) $MgCl_2$ with 100 ml of 0·02 (M) $H_2C_2O_4$. Would MgC_2O_4 be precipitated under this condition ? Given S.P. of $MgC_2O_4 = 8{\cdot}6 \times 10^{-5}$.

11. Calculate the solubility product of Ag_2CrO_4 (Mol.wt.=332). Given its solubility is $2{\cdot}5\times10^{-2}$ g/litre.
[***Ans.*** $1{\cdot}7 \times 10^{-12}$]

12. The solubility product of AgCl is $1{\cdot}45 \times 10^{-4}$ at 373 K. Find its solubility in moles per litre.
[***Ans.*** $1{\cdot}2 \times 10^{-2}$]

13. Solubility product of CaF_2 is $3{\cdot}9 \times 10^{-11}$ at 291 K. What is its solubility in 1 litre of (N/10) NaF solution ?
[***Ans.*** $2{\cdot}3 \times 10^{-7}$ g/litre]

14. The solubility product of PbS is $4{\cdot}2 \times 10^{-28}$ at 298 K. Calculate the concentration of S^{--} ion which is required to precipitate PbS from a solution having $[Pb^{++}] = 1 \times 10^{-3}$ (M).
[***Ans.*** $S^{--} > 4{\cdot}2 \times 10^{-25}$ (M)]

15. If the solubility of AgCl in water be $1{\cdot}3 \times 10^{-5}$ mole per litre, what will be its solubility in 0·1 (M) NaCl medium ?
[***Ans.*** $1{\cdot}7 \times 10^{-9}$ mole/litre]

16. What volume of 0·1M sodium formate solution be added to 50 ml of 0·05M formic acid to produce a buffer solution of pH 4 ? pK_a for formic acid is 3·8.
[***Ans.*** 39·62 ml] *[Roorke '90]*

17. A base BOH has K_b = 8·1 × 10^{-8}. In what amount should 0·02M HCl and 0·02M of BOH be mixed to make 200 ml of a buffer of pH 7 ? [*Ans.* Vol. of HCl = 61·8 ml, vol. of base = 138·2 ml]

18. How many moles of sodium propionate should be added to one litre of an aqueous solution containing 0·02 mole of propionic acid to obtain a buffer solution of pH 4·75? What will be the pH if 0·01 mole of HCl is dissolved in the above buffer solution? Compare the last pH value with the pH of 0·01 molar HCl solution. Dissociation constant of propionic acid K_a at 25°C = 1·34 × 10^{-5}.
[*Ans.* (i) 1·507 × 10^{-2} mol., pH = 4·09] [*I.I.T. '81*]

19. What will be the pH of the solution when 0·2 mole of HCl is added to 1 litre of a solution containing (i) 1M each of acetic acid and acetate ion, (ii) 0.1M each of acetic acid and acetate ion? The dissociation constant of acetic acid is 1·8 ×10^{-5}. [*Ans.* (i) pH = 4·568, (ii) pH = 1] [*I.I.T. '87*]

20. The solubility product of $BaSO_4$ is 1·5 × 10^{-9}. Find out its solubility in (i) Pure water, (ii) 0·1M $BaCl_2$. [*Ans.* 3·87 × 10^{-5} mol/litre; 1·5 × 10^{-8} mol/litre] [*Roorke '89*]

21. What is the pH of an equimolar mixture of CH_3COONa and CH_3COOH buffer solution?
[*Ans.* pH = pK_{CH_3COOH} = 4·74] [*W.B.J.E.E. '93*]

22. The solubility product of AgCl is 2·8 × 10^{-10} at 25°C. Calculate the solubility of AgCl in 0·1 M $AgNO_3$ solution. [*Ans.* 2·8 × 10^{-9}mol/lit]

23. Calculate the concentrations of Mg^{2+} and OH^- ions in a saturated solution of $Mg(OH)_2$. Solubility product of $Mg(OH)_2$ is 9 × 10^{-12}. [*Ans.* 1·31 × 10^{-4} M, 2·62 × 10^{-4}M]

24. The solubility product of $PbBr_2$ is 8 × 10^{-3}. If the salt is 80% dissociated in saturated solution, find the solubility of the salt. [*Ans.* 12·45 g/lit]

25. A buffer solution of acetic acid and sodium acetate of 1 M concentration was prepared and its pH was found to be 4·74. Calculate pH of the system when (i) 0·01 mole of HCl is added to a litre of the above solution, (ii) 0·01 mole of NaOH is added per litre of the above solution. (K_a = 1·8 × 10^{-5})
[*Ans.* (i) 4·73, (ii) 4·75]

26. An acid type indicator HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio [In^{-1}/HIn] is greater than 10 or smaller than 0·1. What would be the minimum changes in the pH of the solution to observe a complete colour changes? [Given K_a = 1 × 10^{-5}] [*Ans.* pH changes from 4 to 6] [*I.I.T. 1997*]

27. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2·0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12·0). [*Ans.* pH = 8] [*I.I.T. 1998*]

CONDUCTANCE 12

The flow of electric current in a conductor is a function of *e.m.f* or electrical potential difference. This is the basis of Ohm's law which states,

'The ratio of the potential difference [*e.m.f (E)*] between any two points in a metallic conductor and the current (*I*) flowing through it, is constant and is equal to the resistance (*R*) between the two points', thus,

$$\frac{E}{I} = R \qquad \text{or,} \qquad E = I.R.$$

where, E = e.m.f. I = current, and R = resistance.

12.1. Conductance of solution—electrolytic conductance.

The current (I) flowing through a solution is directly proportional to the potential difference (E) between the electrodes dipping in it.

Now by applying Ohm's law, we get

$$\text{Resistance of a solution } R = \frac{E}{I}$$

Electrolytic conductance arises due to the mobility of free ions. Metallic conductor resists the flow of electricity, but the electrolytic solutions allow the electric current to flow through them. Thus conducting power is the important value in electrochemistry.

- *The conductance (G) of a conductor is the reciprocal of its resistance (R).*

$$\text{Thus, } conductance\ (G) = \frac{I}{R}$$

Since the unit of resistance is Ohm, its reciprocal—the conductance, is assigned the units of reciprocal Ohm i.e., *Ohm*$^{-1}$ or *mohs* and is denoted as Ω^{-1}.

The conductance of an electrolyte increases with the increase of temperature due to the increased movement of the ions. Smaller viscosity and lesser solvation of the ions help to increase the conductance.

We know that, the resistance (*R*) of any uniform conductor is directly proportional to its length (*L*) and inversely proportional to the area of its cross-section (*A*).

$$\text{Mathematically, } R \propto L \text{ when } A \text{ is constant}$$

$$\text{and } R \propto \frac{1}{A} \text{ when } L \text{ is constant}$$

$$\text{or } R = \frac{\rho L}{A} \text{ (where } \rho \text{ is constant)} \quad \ldots \quad (1)$$

The proportionality constant ρ (rho) is called the *resistivity* or *specific resistance* of the material of which the conductor is made.

$$\text{From (1) we get, } \rho = \frac{RA}{L} \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Now, if $L = 1$ cm, $A = 1\ \text{cm}^2$, then $\rho = R$.

Thus, *specific resistance* (ρ) *or resistivity of the material of a conductor is the resistance of the conductor whose length is 1 cm and area of cross-section is 1 square cm.*

In other words, *it is the resistance between the two opposite sides of a cube of the material whose sides are of 1 cm.* Its unit is **ohm-cm.**

12.2. Specific conductance.

The reciprocal of the specific resistance is called specific conductivity.

- *It is defined as the conductance offered by that portion of the solution which is enclosed between two parallel plates as electrodes, each of area 1 square cm and separated by a distance of 1 cm :*

In fact, it is the *conductivity of unit cube of the solution.*

Specific conductance = conductance of the unit cube of a solution.

Specific conductance is denoted by K

$$K = \frac{1}{\rho} = \frac{1}{R} \times \frac{L}{A} = \frac{L}{RA} \quad \ldots\ldots\ldots\ldots(3)$$

$$\text{Thus unit of specific conductance } K = \frac{\text{cm}}{\text{ohm} \times \text{cm}^2}$$

$$= \text{ohm}^{-1}\ \text{cm}^{-1} \text{ or mho cm}^{-1}$$

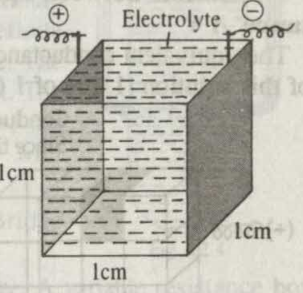


Fig. 12.1

Specific conductance (K) depends upon various factors e.g.,

(i) *concentration of the solution,* (ii) *the temperature,* (iii) *valency of the carrier ion,* (iv) *speed of the ion.*

12.3. Equivalent conductance.

- *The equivalent conductance of an electrolyte is the conductance of that volume of solution, which contains one gram-equivalent of the electrolyte and is placed between two parallel electrodes of indefinite dimensions placed one cm apart.*

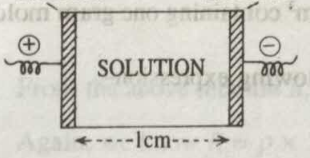


Fig. 12.2

It is represented by Λ (Lambda) and is obtained by multiplying the specific conductance (K) by the volume in ml, which contains one gram equivalent of the given electrolyte i.e., by $\frac{1000}{c}$, where c is the number of gram equivalents of the solute per litre of the solution.

$$\Lambda = V\,K = \frac{1000\,K}{c}$$

- **Units of Λ :**

$$\text{Here, the unit of } \frac{1000}{c} = \frac{\text{cm}^3}{\text{eqv}} = \text{cm}^3\ \text{eqv}^{-1} \text{ and of } K = \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\therefore\ \Lambda = \frac{1000\ K}{c} = \text{cm}^3\ \text{eqv}^{-1} \times \text{ohm}^{-1}\ \text{cm}^{-1} = \text{cm}^2\ \text{eqv}^{-1}\ \text{ohm}^{-1}$$

- **Significance of Λ :**

Let us consider a cell, the area of base of which is 1 cm^2 and the height of which is very high. The opposite walls of the cell act as electrodes.

Now, the cell is filled with an electrolyte to a height of 1 cm. The resistance of the cell is measured. We know $K = \frac{1}{R}$ i.e., reciprocal of the measured resistance is the specific conductance K.

The cell is now filled with a given volume of the solution containing 1 gram equivalent of the electrolyte. The height of the solution will be V cm in the cell and $\frac{1}{R}$ of such cell is the equivalent conductance.

- **Relation between specific conductance (K) and equivalent conductance Λ :**

The equivalent conductance of 1 (N) NaCl solution, is the conductance of 1 litre of this solution [1 litre of 1 (N) NaCl solution contains 1 gram equivalent of NaCl] placed between two large electrodes placed 1 cm apart. This volume i.e., 1000 ml will cover 1000 cm^2 of the surface of each of the electrodes. This also means that, the electrodes will enclose 1000 unit cubes of the solution.

Specific conductance is the conductance of each unit cube, so that the equivalent conductance of solution will be 1000 times that of specific conductance ($\Lambda = 1000\ K$). The relation between specific conductance and equivalent conductance is shown schematically by the figure given here.

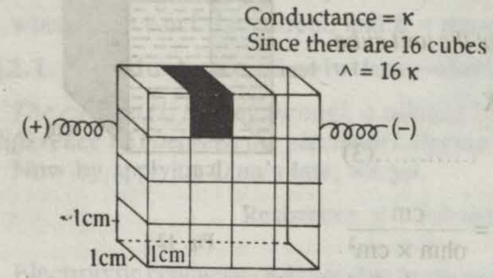


Fig. 12.3 : Relation between K and Λ

12.4. Molar conductance.

- *The conductance of a solution containing one gram mole of the electrolyte per litre, the solution being placed between two parallel electrodes 1 cm apart, is called molar conductance.* Molar conductance of a solution is denoted by μ.

$$\mu = K \times V$$

where K = specific conductance and V = volume in cm^3 containing one gram mole of the electrolyte.

Molecular conductance can also be given by the following expression–

$$\mu = \frac{1000\ K}{c'}$$

where c' is the molarity or molar concentration.

- **Unit of molar conductance :**

$$\text{Molar conductance } \mu = \frac{1000 \times K}{c'}$$

$$\therefore\ \text{Unit of molar conductance} = \frac{\text{ohm}^{-1}\ \text{cm}^{-1} \times \text{cm}^3}{\text{gm mole}} = \text{ohm}^{-1}\ \text{cm}^2\ (\text{gm-mole})^{-1}$$

if $$x = \frac{\text{Molecular wt. of the electrolyte}}{\text{Equivalent wt. of the electrolyte}}$$

$$\therefore \; \mu = \text{equivalent conductance} \times x$$

When equivalent weight = molecular weight, then, $\Lambda = \mu$ i.e., equivalent conductance of the electrolyte is the same as that of its molecular conductance.

12.5. Measurement of conductance.

The specific conductance of a solution is not measured directly. The solution is taken in a container known as *conductance cell* and its resistance is measured using Wheatstone's Bridge principle, since the solution also obeys Ohm's law.

A conductivity cell consists of a pyrex glass bottle of suitable capacity closed by a glass stopper. Two platinum electrodes coated with platinum black are placed at a definite distance apart and fused to opposite walls of the bottle. The distance between the two electrodes in a cell is constant. The two platinum wires are connected to the two arms of the bottle outside which contains mercury for contact with electric circuit.

A diagramatic representation of the Wheatstone Bridge containing the conductivity cell is given in Fig 5.

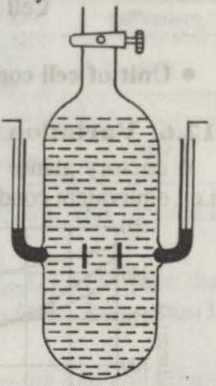


Fig. 12.4

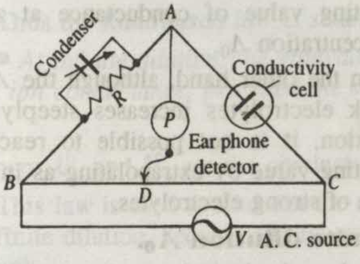


Fig. 12.5

The conductance cell forms one arm *AC* of the bridge. A variable resistance box *R* forms the second arm *AB*, while *BD* and *DC* form a calibrated slide wire resistance and act as the third and fourth arm respectively. A valve oscillator *V* across *BC* supplies alternating current into the circuit. A head phone *P* is connected across *AD* which indicates the null point i.e., the point of balance. A variable condenser is connected in parallel with the variable resistance *R*. When the position of contact *D* is adjusted properly, minimum sound is audible by the head phone *P*. At this condition,

$$\frac{R}{DB} = \frac{R_{cell}}{DC}$$

From the above relation R_{cell} can be found out since other 3 quantities are known.

Again, we know $R = \rho \times \frac{L}{A}$ or $\frac{1}{\rho} = \frac{1}{R} \cdot \frac{L}{A}$

or, Specific conductance (K) = conductance $\times \frac{L}{A}$

L/A = cell constant.

or K = observed conductance × cell constant of the conductivity cell.

- **Cell constant :** If the resistance of the electrolyte in the conductivity cell be R and specific conductance K, then cell constant is related to R as follows—

$$K = \frac{\textit{Cell constant}}{R} \quad \ldots \quad \ldots \quad (7)$$

$$\text{or, cell constant} = K \times R$$

Again, if the conductivity cell is a tube of uniform cross-section with the electrodes at its ends, then,

$$\text{Cell constant} = \frac{\textit{Length}}{\textit{Area of cross section}}$$

- **Unit of cell constant** $= \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}$

12.6. Variation of equivalent conductance with concentration.

A cursory glance at the graph (Fig. 12.6) given here, showing the variation of Λ i.e., equivalent conductance with $\sqrt{c}$ i.e., concentration, indicates that the equivalent conductance varies appreciably with molar concentration. With the decrease of concentration, the equivalent conductance increases but the behaviour of strong and weak electrolytes are quite different in this respect.

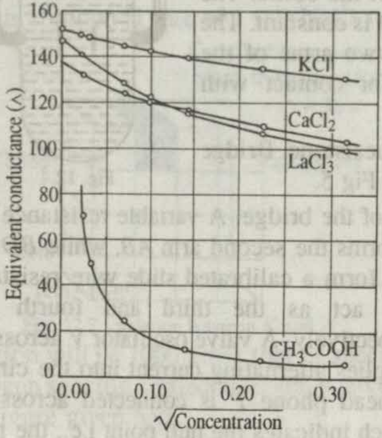


Fig. 12.6

On dilution Λ of a strong electrolyte rapidly approaches a value, close to the limiting value of conductance at zero concentration Λ_0.

On the other hand, although the Λ of weak electrolytes increases steeply on dilution, it is not possible to reach a limiting value by extrapolating as in the case of strong electrolytes.

12.7. Equivalent conductance at infinite dilution Λ_0.

A look on the plot of Λ *vs* $\sqrt{c}$ for strong and weak electrolytes, shows that, for strong electrolytes in dilute solution the graph is almost linear.

Kohlrausch proposed the following

$$\Lambda = \Lambda_0 - b\sqrt{c} \quad \text{where, } b \text{ is a constant.}$$

Extrapolation of plot to infinite dilution i.e., when $\sqrt{c} = 0$, or knowing the slope of the linear portion of the curve, one can find out the value of equivalent conductance at infinite dilution. This is the value of conductance of the electrolyte when the constituent ions are so far apart, that they do not interact at all.

It should be noted that, although Λ_0 is frequently referred to as the conductance at infinite dilution, it is not equal to the conductance of pure solvent i.e., water. Consequently, at high dilution, conduction due pure electrolyte is the difference of the conductance of the solution and that of pure solvent (water).

$$K_{\text{Solute}} = K_{\text{Solution}} - K_{\text{Solvent}}$$

12.8. Kohlrausch's law of independent migration of ions.

Kohlrausch measured the equivalent conductance of a number of strong electrolytes and observed that the difference between the equivalent conductivity at infinite dilution of pairs of salts having any ion common, is constant at a definite temperature and for a definite solvent. An examination of the following table, reveals the truth of the observation.

Λ_0 Values for pairs of electrolytes at 25°C.

Electrolytes	Λ_0 at 25°C	Difference
KCl	149.9	34.9
LiCl	115.0	
KNO_3	145.0	34.9
$LiNO_3$	110.01	

Electrolytes	Λ_0 at 25°C	Difference
KOH	271.5	34.8
LiOH	236.7	
$KClO_4$	140.0	34.9
$LiClO_4$	105.08	

The constant difference of about 34.9 is always found between K and Li salts of the same acid radical at infinite dilution.

It can thus be concluded that the conductance of K^+ ion ($\Lambda^0_{K^+}$) is 34.9 more than that of Li^+ ion ($\Lambda^0_{Li^+}$), because the anion is same. On the basis of this observation he concluded that,

At infinite dilution, each ion migrates independently of its co-ion and contributes a definite share to the total equivalent conductance of the electrolyte. This contribution is independent of the other associated ion.

Thus the *Kahlrausch law* is stated as—

- *At infinite dilution, the equivalent conductance of any electrolyte is the sum of its ion conductance, provided the solvent and temperature remain same.*

$$\Lambda_0 = \lambda^0_+ + \lambda^0_-$$

where λ^0_+ and λ^0_- are the conductance of cation and anion respectively.

This law is used to find out the equivalent conductance of a weak electrolyte at infinite dilution, because in this case Λ_0 can not be found out by extrapolating the graph.

12.9. Ionisation of weak electrolyte—degree of dissociation.

The degree of dissociation of a weak electrolyte e.g., CH_3COOH, NH_4OH etc., can not be evaluated from the measured conductance of the electrolyte (Λ) and the equivalent conductance at infinite dilution (Λ_0) as in case of strong electrolyte.

At infinite dilution, the equivalent conductance of an electrolyte is given by the expression—

$$\Lambda_0 = n_+ z_+ e\, u_+ + n_- z_- e\, u_- \; \ldots \qquad \ldots \qquad (11)$$

where, n_+ and n_- are the number of cation and anion respectively. u_+ and u_- are the velocities of cations and anions respectively. z_+ and z_- being valencies of cation and anion respectively. e = unit charge (96500 C).

If α be the degree of dissociation at a particular concentration (c gram equivalent per litre).

$$\Lambda_0 = \alpha\, n_+ z_+ e\, u_+ + \alpha\, n_- z_- e\, u_- \quad \ldots \quad (12)$$

Now dividing (12) by (11) we get,

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (13)$$

Equation (13) is not applicable to strong electrolyte in which dissociation is practically complete. This equation is applicable only to find out α of weak electrolyte.

12.10. Ionic mobility.

- *The velocity in cm/sec with which an ion moves, when the driving force is unit potential gradient (i.e., under one volt per cm) is called absolute velocity of ion or mobility of ion.*

If U = ionic mobility, and λ = ion conductance then, it can be shown that,

$$U = \frac{\lambda}{F} \qquad \text{or, } \lambda = U.F \quad \ldots \quad \ldots \quad (14)$$

i.e., ionic conductance (λ) = *ionic mobility × Faraday,*

$$\text{Thus,} \qquad \lambda_+ = U_+ \times F \text{ and } \lambda_- = U_- \times F \quad \ldots \quad (15)$$

12.11. Transport number.

The total current carried by a solution of an electrolyte having only two types of ions, is equal to the sum of the current carried by the cations and anions.

Total current carried by the electrolyte

$$= Z_+ c_+ U_+ + Z_- c_- U_-$$

where, Z and c be the charges and equivalent concentrations respectively and + and − signs denote cation and anion respectively.

- *Transport number (t) is defined as the fraction of the total current carried by the ions. The ions which move faster, carry the larger fraction of electricity through the solution.*

$$t_+ = \frac{Z_+ c_+ U_+}{Z_+ c_+ U_+ + Z_- c_- U_-} \quad \ldots \quad \ldots \quad (16)$$

$$\text{and} \quad t_- = \frac{Z_- c_- U_-}{Z_+ c_+ U_+ + Z_- c_- U_-} \quad \ldots \quad \ldots \quad (17)$$

(i) In case of electrolytes like KCl, $MgSO_4$, etc., where $Z_+ c_+ = Z_- c_-$,

$$t_+ = \frac{U_+}{U_+ + U_-} \text{ and } t_- = \frac{U_-}{U_+ + U_-} \quad \ldots \quad (18)$$

$$\text{Thus, } t_+ + t_- = \frac{U_+}{U_+ + U_-} + \frac{U_-}{U_+ + U_-} = \frac{U_+ + U_l}{U_+ + U_-} = 1 \quad \ldots \quad (19)$$

The relation between transport number and ionic conductance is given by

$$t_+ = \frac{\lambda^0{}_+}{\Lambda^0} \text{ and } t_- = \frac{\lambda^0{}_-}{\Lambda^0} \quad \ldots \quad \ldots \ldots \quad (20)$$

This relation is applicable at infinite dilution

Λ_0 = equivalent conductance at infinite dilution.

12.12. Solubility and equivalent conductance.

The solubility and solubility product of a sparingly soluble salt can be evaluated by measuring their conductance. Since the solubility of these salts are very low, their measured equivalent conductance may be regarded as equal to that of infinite dilution i.e., Λ^0 e.g.,

$$\Lambda^\circ_{AgCl} = \frac{K_{AgCl(S)} \times 1000}{c}$$

Here, $K_{AgCl(S)} = K_{(Solution)} - K_{water}$

c = concentration of the electrolyte in gram equivalent per litre

Again, $\Lambda^\circ_{AgCl} = \lambda^\circ_{Ag^+} + \lambda^\circ_{Cl^-}$

$\Lambda^\circ_{Ag^+}$ and $\lambda^\circ_{Cl^-}$ can be known from literature and c can be found out.

$\therefore$ If K_s = Solubility product.

Thus, $K_S = c^2$ thus solubility product of silver chloride can be found out.

- **Numerical problems :**

1. *When a conductance cell is filled with 0.02 (M) KCl solution having a specific conductance of 2.768×10^{-3} ohm^{-1} cm^{-1}, it had resistance 82.4 ohm at 25°C. When filled with 0.005 (N) K_2SO_4, it had a resistance of 310 ohm. Calculate the cell constant and specific conductance of K_2SO_4 solution.*

Ans. We know, cell constant = specific conductance × resistance

$$= 2.768 \times 10^{-3} \times 82.4$$
$$= 0.2281 \text{ cm}^{-1}$$

Again, specific conductance $= \dfrac{\text{Cell constant}}{\text{Resistance}}$

$$= \frac{0.2281 \text{ cm}^{-1}}{310} = 7356 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

2. *Calculate the equivalent conductance of 0.005 (N) Li_2SO_4 solution, if its specific conductance is 6.997×10^{-4} ohm^{-1} cm^{-1} at 25°C.*

Ans. We know, $\Lambda = \dfrac{1000K}{c} = \dfrac{1000 \text{ cm}^3\text{lit}^{-1} \times 6.997 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}}{0.005 \text{ eqv lit}^{-1}}$

$$= 139.9 \text{ cm}^2 \text{ eqv}^{-1} \text{ ohm}^{-1}$$

3. *Calculate the equivalent conductance of acetic acid at infinite dilution at 25°C. Given the Λ^0 values of HCl, NaCl and CH_3COONa are 426.1, 126.5 and 91.0 respectively.* [*I.S.C.* '82]

Ans. We know, $\Lambda_{o(HCl)} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}$

$$\Lambda_{o(NaCl)} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$$
$$\Lambda_{CH_3COONa} = \lambda^\circ_{Na^+} + \lambda^\circ_{CH_3COO^-}$$

Now, $(\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}) + (\lambda^\circ_{Na^+}\ \lambda^\circ_{CH_3COO^-}) - (\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}) = \lambda^\circ_{H^+} + \lambda^\circ_{CH_3COO^-}$

or, $(\Lambda^\circ_{HCl} + \Lambda^\circ_{CH_3COONa} - \Lambda^\circ_{NaCl} = \Lambda^\circ_{CH_3COOH}$

or, $426.1 + 91.0 - 126.5 = \Lambda_{0\ CH_3COOH}$

or, $\Lambda_{0\ CH_3COOH} = 390.6\ cm^2\ eqv^{-1}\ ohm^{-1}$

4. *The equivalent conductance of a 0.001028 (N) CH_3COOH solution is found to be 96.3 $cm^2\ eqv^{-1}\ ohm^{-1}$ and the equivalent conductance of the same solution of infinite dilution is 781.2 $cm^2\ eqv^{-1}\ ohm^{-1}$. Calculate the ionisation constant of acetic acid.*

Ans. We know, $\alpha = \Lambda/\Lambda_0 = 96.3/781.2 = 0.1232$

From Ostwald dilution law we get

$$K_{CH_3COOH} = \frac{\alpha^2 c}{1 - \alpha} = \frac{(0.1232)^2 \times (0.001028)}{0.8768} = 1.78 \times 10^{-5}$$

5. *Calculate the equivalent conductance of CH_3COONa at 25°C using the following data—*

Equivalent conductance of HCl and CH_3COOH at infinite dilution are 426.1 and 91.0 respectively. The transport number of H^+ ion = 0.82 and Na^+ ion = 0.55.

Ans. Since the transport number of Na^+ in CH_3COONa is 0.55, the transport number of CH_3COO^- is $1 - 0.55 = 0.45$. Now using equation we get,

$$\lambda^\circ_{H^+} = t_{H^+} \times \Lambda_{0\ HCl} = 0.82 \times 426.1 = 349.4$$

$$\lambda^\circ_{CH_3COO^-} = t_{CH_3COO^-} \times \Lambda_{0\ CH_3COONa} = 0.45 \times 91 = 40.9$$

$$\therefore\ \Lambda^\circ_{CH_3COOH} = \lambda^\circ_{H^+} + \lambda^0_{CH_3COO^-} = 349.4 + 40.9 = 390.3$$

6. *A 0.01(M) KOH solution offered a resistance of 31.6 ohm in a conductivity cell at 25°C. If the cell constant of the cell is 0.367 cm^{-1}, calculate the molar conductance of KOH solution.*

Ans. Specific conductance $K = \dfrac{\text{Cell constant}}{\text{Resistance}}$

$$= \frac{0.367\ cm^{-1}}{31.6\ ohm} = 0.0116\ ohm^{-1}\ cm^{-1}$$

$$\text{Molar conductance } (\mu) = \frac{K \times 1000}{\text{molarity}} = \frac{0.0116\ ohm^{-1}\ cm^{-1} \times 1000\ cm^3}{0.01}$$

$$= 1.16\ ohm^{-1}\ cm^2\ \text{gram mole}^{-1}$$

7. *A 0.1(N) solution of a weak organic acid has a specific conductance of 0.00313 $ohm^{-1}\ cm^{-1}$. If the degree of dissociation of the acid be 0.0447, find the equivalent conductivity of the solution at infinite dilution.*

Ans. $\Lambda = \dfrac{1000K}{c} = \dfrac{1000\ cm^3 \times 0.00313\ ohm^{-1}\ cm^{-1}}{0.1}$

or, $\Lambda = 31.3\ ohm^{-1}\ cm^2\ gm\ eqv^{-1}$

Again, $\alpha = \dfrac{\Lambda}{\Lambda_0}$ or, $\Lambda_0 = \dfrac{\Lambda}{\alpha} = \dfrac{31.3}{0.0447}$

or $\Lambda_0 = 700.22\ ohm^{-1}\ cm^2\ eqv^{-1}$

8. *Calculate the ionic conductance of Cd^{2+} ion assuming its velocity to be 2.74×10^{-4} cm·sec^{-1}, the potential gradient being 1 volt cm^{-1}.*

Ans. $\lambda^0_{Cd^{2+}} = Z_+ \, U_+ \, F$ where Z_+ is the valency of Cd^{++} ion.

or, $\lambda^\circ_{Cd^{2+}} = 2 \times 2.74 \times 10^{-4} \times 96500$

$= 52.88$ ohm^{-1} cm^2 mole^{-1}

9. *The equivalent conductance of 0.1(N) $ZnCl_2$ solution is 97.1 ohm^{-1} cm^2 eqv^{-1} at 298K. A cell with electrodes each of 3.0 cm^2 in area and 1 cm apart, is filled with (N) $ZnCl_2$ solution. How much current will flow if the potential difference between the two electrodes is 8 volt?*

Ans. Cell constant of the cell $= \dfrac{\text{length}}{\text{area}} = \dfrac{1}{3} = 0.333 \text{ cm}^{-1}$

We know, $K = \dfrac{\Lambda . c}{1000} = \dfrac{97.1 \times 0.1}{1000}$

$= 0.00971 \text{ ohm}^{-1} \text{ cm}^{-1}$

Conductance $= \dfrac{K}{\text{cell constant}} = \dfrac{0.00971}{0.333} = 0.02913 \text{ ohm}^{-1}$

Again, resistance $= \dfrac{1}{\text{conductance}} = \dfrac{1}{0.02913} \text{ ohm}^{-1}$

Current in amp = P.D/resistance

$= \dfrac{8}{1/0.02913} = 0.23305$ amp

10. *A saturated solution of $BaSO_4$ at 25°C offered a specific conductance 3.65×10^{-6} ohm^{-1} cm^{-1}. The specific conductance of water used for preparing the solution was 1.25×10^{-6} ohm^{-1} cm^{-1}. Equivalent conductance of $BaCl_2$, K_2SO_4 and KCl at infinite dilution are 120.3, 132.3 and 129.6 respectively at 25°C. Calculate the solubility of $BaSO_4$ in water at 25°C.*

Ans. From Kohlrausch law of independent migration of ion we can write,

$$\lambda^0_{Ba^{++}} + \lambda^0_{SO_4^{=}} = \Lambda_{0\ BaSO_4}$$

$$\lambda^0_{1/2\ Ba^{++}} + \lambda^0_{Cl^-} = 120.3$$

$$\lambda^0_{K^+} + \lambda^0_{1/2SO_4^{=}} = 132.3$$

$$\lambda^0_{K^+} + \lambda^0_{Cl^-} = 129.6$$

$$\therefore\ \lambda^0_{1/2\ Ba^{++}} + \lambda^0_{1/2SO_4^{=}} = 120.3 + 132.3 - 129.6 = 123$$

or, $\Lambda^0_{BaSO_4} = 123$

Now, $K_{BaSO_4} = K_{Soln} - K_{water}$

$= 3.65 \times 10^{-6} - 1.25 \times 10^{-8}$

$= 2.4 \times 10^{-6}$ ohm^{-1} cm^{-1}

Since the solution is very dilute, equivalent conductance Λ of $BaSO_4$ is equal to Λ_0 i.e., equivalent conductance at infinite dilution.

$$\Lambda_0 = \frac{1000\ K}{c} \quad \text{or,} \quad c = \frac{1000K}{\Lambda_0}$$

$$\therefore \text{ Concentration } c \text{ in gm eqv lit}^{-1} = \frac{1000 \times 2.4 \times 10^{-6}}{123} = 195 \times 10^{-5} \text{ gm eqv lit}^{-1}$$

The equivalent weight of $BaSO_4$ = 116.7

Hence the solubility of $BaSO_4 = 1.95 \times 10^{-5} \times 116.7$

$= 2.2756 \times 10^{-3}$ gram per litre

• Exercises •

1. Explain the significance and inter relationship of the following :

Transport number, ionic mobilities and equivalent conductance at infinite dilution.

2. Define specific and equivalent conductance of a solution of any electrolyte. How are they related? Show with the help of plots how the equivalent conductance of strong and weak electrolytes vary with concentration. What do you mean by equivalent conductance at infinite dilution? [*C.U. B.Sc. 1993*]

3. State and explain Kohlrausch's Law of independent migration of ion.

4. Write the unit of the following—

(i) Specific conductance, (ii) Equivalent conductance, (iii) Transport number, (iv) Cell constant, (v) Ionic mobility.

5. Write brief notes on—(i) Cell constant (ii) Specific conductance (iii) Molar conductance.

6. Prove that the cell constant is approximately equal to the distance between the two electrodes divided by the mean area of the electrodes.

7. What do you mean by degree of dissociation of a substance in solution? Explain how it can be determined from conductivity measurement.

8. Is it possible to determine equivalent conductance of infinite dilution (Λ_0) for HCl and CH_3COOH by the same experimental procedure?

9. Explain why?

(i) The specific conductivity of a solution decreases on dilution.

(ii) Equivalent and molar conductance increase on dilution.

(iii) A galvanometer is not used for detecting null point in the measurement of resistance of a solution.

(iv) Electrolytic conduction is due to the migration of ions in solution.

(v) Conductivity depends upon both the speed of the ion and total number of ions.

10. Among the various alternatives given below select the correct answer—

(i) At infinite dilution, the contribution of cation and anion to the equivalent conductance

(a) depends upon the nature of solvent (b) independent of each other (c) depends on each other (d) none of the above. [*Ans.* (b)]

(ii) The conductance due to all the ions present in the solution of one gm equivalent of an electrolyte is

(a) Molecular conductance (b) Ionic mobility (c) Specific conductance (d) Equivalent conductance. [*Ans.* (d)]

(iii) With the rise in temperature conductivity of metals

(a) Decreases (b) Increases (c) Remains unchanged (d) May decrease or increase. [*Ans.* (a)]

(iv) Which of the following equation is correct

(a) $\Lambda = 1000$ K (b) Cell constant = $\frac{\text{Legth}}{\text{Area}}$ (c) Conductance = $K \times$ cell constant (d) $\frac{\Lambda}{\Lambda_0} = 1 + \alpha$. [*Ans.* (b)]

(v) The cell constant of a cell is 0.88 cm^{-1}. The resistance of the solution is 200 ohm. The specific conductance of the solution is—

(a) 0.0044 $ohm^{-1}\ cm^{-1}$, (b) $17.6 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$, (c) $1.2 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$, (d) $2 \times 10^{-3}\ ohm^{-1}\ cm^{-1}$. [*Ans.* (a)]

Numerical Problems :

1. At 25°C the equivalent conductance of propionic acid at infinite dilution is 385.6 (cm^2 ohm^{-1} eqv^{-1} the ionisation constant is 1.34×10^{-5}. Calculate the equivalent conductance of 0.05(N) solution of propionic acid at the same temperature. [*Ans.* 6.32 cm^2 ohm^{-1} eqv^{-1}]

2. The resistance offered by 0.1 (N) $ZnSO_4$ in a cell was found to be 45 ohm. Calculate the cell constant of the cell if the specific conductance of the cell is 0.01 mho cm^{-1} [*Ans.* 0.45 cm^{-1}]

3. The equivalent conductance of N/50 acetic acid solution is 11.92 mho cm^2 eqv^{-1}. The equivalent ionic conductance at infinite dilution of H^+, CH_3COO^- ions are 360 and 40 respectively. Calculate the dissociation constant of CH_3COOH, [*Ans.* 1.78×10^{-5}]

4. Values of equivalent conductances at infinite dilution of NaCl, NaOH and NH_4Cl are 126.5, 248.7 and 149.9 mho cm^2 respectively. Find the equivalent conductance of NH_4OH at infinite dilution. [*Ans.* 272 mho cm^2 eqv^{-1}] [*I.I.T. '79*]

5. A solution of 0.1 (M) CH_3COOH at 25°C has a specific conductance of 5.226×10^{-4} ohm^{-1} cm^{-1}

(i) Find the equivalent conductance of 0.1M CH_3COOH.

(ii) Find the equivalent conductance of CH_3COOH at infinite dilution. Given K_a of CH_3COOH = 1.8×10^{-5} [*Ans.* (i) 5.226 (ii) 390 ohm^{-1} cm^2 eqv^{-1}] [*I.I.T. '80*]

6. In a particular cell a 0.01 demal solution of KCl gave a resistance of 150 ohm at 298 K, while a 0.01(N) HCl gave a resistance of 51.4 ohm at the same temperature. At 298 K the specific conductance of 0.01 demal KCl solution is 0.0014088. Find the specific and equivalent conductance of HCl. [*Ans.* $K = 0.00411$ ohm^{-1} cm^{-1}, $\Lambda = 411.1$ ohm^{-1} cm^2 eqv^{-1}]

[Hint : 1 demal solution contains 1 mole of solute per litre of the solution at 298K]

7. The equivalent conductance of a 0.014 (N) solution of chloro acetic acid is 109 at 298 K. If equivalent conductance at infinite dilution is 389.5, what is the ionisation constant of chloro acetic acid. [*Ans.* 1.52×10^{-3}]

8. At 298 K, the resistance of a cell filled with 0.01 demal KCl solution is 525 ohm. The resistance of the same cell filled with 0.1 (N) NH_4OH is 2030 ohm. Calculate the degree of dissociation of NH_4OH at this dilution. [*Ans.* 0.0134]

9. In a solution of the salt XY, X^+ migrates 0.6 times slower than Y^- when electrolysed. Calculate the transport number of Y^-. [*Ans.* 0.625]

10. The equivalent conductance of NaCl at infinite dilution is 126. If the ionic mobility of Na^+ ion is 5×10^{-4} cm sec^{-1}, calculate the ionic conductivity of Na^+ ion and its transport number. [*Ans.* Ionic conductivity = 48.25 ohm^{-1}, $t = 0.383$]

11. Calculate the percentage of ionisation of N/5000 CH_3COOH solution, if its equivalent conductance is 50. $\Lambda_0 = 350$. [*Ans.* 14.28%]

12. A 0.01 (M) KOH solution offered a resistance of 31.6 ohm in a conductivity at cell 25°C. If the cell constant of the cell is 0.367 cm^{-1}, calculate the molar conductance of KOH solution. [*Ans.* 232 ohm^{-1} cm^2 mole^{-1}]

13. At 25°C, the specific conductance of a saturated solution of AgBr is 1.576×10^{-6} ohm^{-1} and that of water used is 1.519×10^{-6} ohm^{-1}. On the assumption that AgBr is dissociated, calculate the solubility, solubility product of AgBr. Given that the equivalent conductance of KBr, KNO_3 and $AgNO_3$ at infinite dilution are 137.4, 131.3 and 121.0 respectively. [*Ans.* Solubility : 4.49×10^{-7} gm eqv lit^{-1}; Solubility product : 2.03×10^{-13}]

14. The equivalent conductance of water at 18°C is 0.684×10^{-6} ohm^{-1} cm^2 eqv^{-1}. The ionic conductance of H^+ and OH^- ions at infinite dilution are 315.2 and 173.8 respectively. Calculate the ionic product of water (K_w) at this temperature. [*Ans.* 0.597×10^{-14}]

15. The following table gives the equivalent conductance data at infinite dilution at 25°C (in ohm^{-1} cm^2 eqv^{-1})

Electrolyte	Λ_0
Sodium butyrate	82.6
Hydrochloric acid	426.2
Sodium chloride	126.5

Calculate the equivalent conductance of butyric acid at infinite dilution at 25°C. [*Ans.* 382.3 ohm^{-1} cm^2 eqv^{-1}]

16. In a conductivity cell, the two platinum electrodes each of area 20 cm^2 are fixed 1 cm apart. The cell contained 0.01 (N) KCl solution, so that the two electrodes are just half filled. When connected with a Wheatstone bridge, the solution gave a resistance of 50 ohm. Find the equivalent conductance of the solution. [*Ans.* 200 ohm^{-1} cm^2 eqv^{-1}]

17. The equivalent conductance of NaF in 0.1 (N) solution is 83.5 ohm^{-1} cm^2 eqv^{-1}. The salt may be taken as 92% dissociated. If the transport number of Na^+ ion is 0.45, calculate the mobilities of the sodium and fluoride ions. [*Ans.* $Na^+ = 4.23 \times 10^{-4}$, $F^- = 5.17 \times 10^{-4}$ cm^2 $volt^{-1}$ sec^{-1}]

18. The ionic conductance of NH_4^+ ion at infinite dilution is 73.51 ohm^{-1} at 298 K. A solution of NH_4Cl is placed between two electrodes 8.5 cm apart and connected to a potential of 18 volts. What will be the displacement of NH_4^+ ion in 100 minutes under the applied potential? [*Ans.* 9.678×10^{-4} cm]

[**Hints** : Displacement = ionic mobility × potential gradient × time

Again, ionic mobility = $\dfrac{\text{ionic conductance}}{96500}$]

APPENDIX

Electronic theory of oxidation and reduction and oxidation number.

[Redox reactions have been discussed in details in our Vol II but frequently we have used the concept of oxidation and reduction in Vol I also. Hence an elementary idea of oxidation number and electronic concept of redox reaction is given for the convenience of the students.]

Oxidation-Reduction and Electronic Idea :

1. Oxidation : *Oxidation is a process where an atom or ion loses electron(s) or oxidation involves loss of electron(s).*

(i) Atoms like Na, Ca, Al etc., lose electron and are converted into their corresponding ions. These atoms are said to be oxidised as they lose electron(s).

$$Na - e \rightarrow Na^+ ; \quad Ca - 2e \rightarrow Ca^{++}$$
$$Al - 3e \rightarrow Al^{+++}$$

(ii) Ions like Fe^{++}, Sn^{++} etc., are oxidised to higher valent ions Fe^{3+} and Sn^{4+} by the loss of electron(s)

$$Fe^{++} - e \rightarrow Fe^{3+}$$
$$Sn^{++} - 2e \rightarrow Sn^{4+}$$

(iii) Anions like chloride, bromide, sulphide etc., lose electron(s) and are oxidised into the corresponding atoms.

$$2Cl^- - 2e \rightarrow Cl_2 ; \quad 2Br^- - 2e \rightarrow Br_2$$
$$S^{--} - 2e \rightarrow S$$

2. Reduction : *Reduction is a process where an atom or ion gains electron(s).* Thus whenever an atom or ion increases its electron number we conclude that the atoms or the ions are reduced.

Thus, (i) Ions like Al^{3+}, Fe^{3+} etc., gain electron(s) and are reduced to metals.

$$Al^{+++} + 3e \rightarrow Al ; \quad Fe^{+++} + 3e \rightarrow Fe$$

(ii) Again some ions by gaining electron(s) are reduced into lower valent ions.

$$Fe^{+++} + e \rightarrow Fe^{++}$$
$$Sn^{++++} + 2e \rightarrow Sn^{++}$$

(iii) Atoms like chlorine, sulphur, oxygen etc., are converted into corresponding anions by gaining electron(s).

$$Cl + e \rightarrow Cl^- \quad S + 2e \rightarrow S^{--}$$
$$O + 2e \rightarrow O^{--}$$

In accordance with this concept, an oxidising agent gains electron(s) and is reduced while a reducing agent loses electron(s) and is oxidised. As a result of this exchange of electron, the valency of the corresponding atoms or ions are changed. The valency of an oxidised atom or ion is increased and the valency of a reduced atom or ion is decreased. Thus, an oxidising agent by gaining electrons from a reducing agent oxidises the latter but itself is reduced, while a reducing agent gives up electron(s) to an oxidising agent and thus, reduces the latter but itself is oxidised.

Oxidising and reducing agents differ among themselves in strength or chemical reactivity. Strong oxidising agents have a pronounced tendency to gain electron(s). Hence all strong oxidising agents must have high electronegativity. In fact as the electronegativity of an atom increases its oxidising power also increases. Strong oxidising agents are able to remove electron(s) from many reducing agents including weak reducing agents which yield electrons reluctantly. Weak oxidising agents can only oxidise strong reducing agents which give up electron easily.

Oxidation-reduction reaction takes place simultaneously :

In every Redox reaction both the oxidant and the reductant occur together because the electron(s) lost by the reducing agent must be accepted by the oxidising agent e.g., when Cl_2 is passed into $FeCl_2$ solution, the colour of the latter changes from light green to yellow.

$$\overbrace{2FeCl_2 + \underbrace{Cl_2 \rightarrow 2FeCl_3}_{+2e}}^{-2e}$$

Ionically :—

$$\begin{array}{llcl} & 2Fe^{++} - 2e & \rightarrow & 2Fe^{+++}\text{ (oxidation)} \\ & Cl_2 + 2e & \rightarrow & 2Cl^-\text{ (reduction)} \\ \text{Adding} & 2Fe^{++} + Cl_2 & \rightarrow & 2Fe^{+++} + 2Cl^- \end{array}$$

Hence it is concluded that oxidation and reduction take place simultaneously.

Oxidation state and oxidation number :

Redox process involving typical covalent compounds can not be explained by electronic approach. Thus burning of C in air or reaction between H_2 and Cl_2 which are typical redox reaction cannot, however, be explained by electronic approach. In order to overcome this difficulty O.C. Johnson introduced a term oxidation number and defined oxidation and reduction in terms of this concept. Oxidation number, in fact, is a measure of the electron control that an atom has in a compound compared to the atom in the pure element. It is due to the difference in electronegativity in a covalent bond $A - B$, the more electronegative atom say A will have larger share on the bonding electron pair $A - B \longleftrightarrow A^{\delta-}B^{\delta+}$. Hence oxidation number of an element in a particular compound is the formal charge either positive or negative which can be assigned to the element taking all the body as ionic. The charges are not real ones. Thus in HCl the formal charge of Hydrogen is δ^+ and Chlorine δ^-. Hence Hydrogen is in +1 oxidation state and Chlorine is in −1 oxidation state. O.C. Johnson defined oxidation number as follows "*Oxidation number of an element is a number which when applied to that element in a particular compound indicates the amount of oxidation or reduction required to convert one atom of the element from the free state into that in the compound. If oxidation is necessary to affect the change, the oxidation number is positive ; if reduction is necessary then oxidation number is negative.*

Oxidation-Reduction and Oxidation number :

Although oxidation number is purely arbitrary in nature, oxidation and reduction process can be very conveniently defined by this concept. According to this concept *oxidation is a process in which the oxidation number of an element is increased, while in reduction the oxidation number of the element is decreased. The oxidation number of oxidising agent is diminished and it is enhanced for a reducing agent in a redox reaction.*

Maximum and minimum oxidation number :

The elements must have a maximum and a minimum oxidation number. The maximum oxidation number of the element is indicated by its position in the group in the periodic table or the total number of electrons in the outermost shell of the atom. Thus the maximum oxidation number of nitrogen is +5 since it occurs in group VB of the periodic table. The electronic configuration of nitrogen is $1s^2\,2s^2\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,1}$ (the total number of electron in the outermost shell being 5). Again the total number of *unpaired* electron in the atom denotes its minimum oxidation number. Thus the minimum oxidation number of nitrogen is −3 as it contains 3 unpaired electrons. Maximum and minimum oxidation numbers of some elements are given below :—

Elements	Maximum Oxidation No.	Minimum Oxidation No.
Sulphur	+6	−2
Phosphorous	+5	−3
Nitrogen	+5	−3
Chlorine	+7	−1
Carbon	+4	−4

Rules for fixing oxidation number of an element :

1. The oxidation number of an element in the free state or uncombined state is 0.

2. The oxidation number of hydrogen is +1 except in ionic hydride where it is −1 e.g., LiH, CaH_2, NaH etc.

3. The oxidation number of oxygen is normally −2, except in peroxide where it is −1. e.g., H_2O_2, BaO_2. The oxidation number of oxygen is positive in F_2O (+2) and F_2O_2 (+1).

4. The oxidation number of a metal is positive and is equal to its valency except in GeH_4 where it is −4 or in $Na[Co(CO)_4]$ where Co is in −1 state.

5. The total oxidation number of a compound is zero and is obtained by adding the oxidation number of each atom in the molecule.

Oxidation number of some elements :

1. *Oxidation number of chlorine in $KClO_4$:*

Let the oxidation number of Cl be x

Total oxidation number of $KClO_4 = (+1) + x + 4(-2) = x - 7$

Since the total oxidation number is 0.

$x - 7 = 0$

or, $x = +7$

Hence oxidation number of chlorine in $KClO_4 = +7$.

2. *Oxidation number of Cr in $Cr_2O_7^{--}$:*

Let the O.N. of Cr be x. The total oxidation number of $Cr_2O_7^{--}$ is—

$2x + 7 \times (-2) = 2x - 14$

The charge of $Cr_2O_7^{--} = -2$

$\therefore\ 2x - 14 = -2$

or, $x = +6$

Hence O.N. of Cr in $Cr_2O_7^{--} = +6$

• Explain with reasons whether the following reactions belong to Redox process or not.

1. Decrease of O. N. = Reduction

$$\overset{+4}{MnO_2} + 4H\overset{-1}{Cl} = \overset{+2}{MnCl_2} + \overset{0}{Cl_2} + 2H_2O$$

Increase of O. N. = Oxidation

Here Mn (IV) state is reduced to Mn (II) state while Cl (−I) state is oxidised to Cl (0) state. Hence the above reaction is a redox reaction.

2. $$\overset{+1}{Na}\overset{-1}{Cl} + \overset{+1}{Ag}\overset{+5}{N}\overset{-2}{O_3} = \overset{+1}{Na}\overset{+5}{N}\overset{-2}{O_3} + \overset{+1}{Ag}\overset{-1}{Cl}$$

Here the O. N. of all the elements remain constant. Hence the above reaction is not a redox reaction.

• INORGANIC CHEMISTRY •

Oxygen, Hydrogen, Water, Hydrogen peroxide and Ozone

1

• OXYGEN (O_2) •

Atomic number = 8 **Atomic weight = 16**
Electronic configuration—$1s^2 . 2s^2 . 2p^4$. **Oxidation No. (−2), (−1), (+2)**
Electronegativity = 3.5

• **Discovery and occurrence** : Scheele, Priestly, and Lavoisier discovered oxygen in 1774. Scheele named the gas '*vital air*'. Lavoisier was the first to prove that the gas helped combustion and respiration and he named it '*oxygen*'. 'Oxygen' means an acid producer because he showed that the products obtained by the chemical combinations of oxygen with non-metals like sulphur, phosphorus, carbon etc., on being treated with water, produced acid.

In free state oxygen exists in air to the extent of about 21% by volume. Free oxygen is also found dissolved in natural waters. It is an essential constituent of water. Most of the minerals found in nature contain oxygen. Sand is nothing but the oxide of silicon (SiO_2). Earth's crust contains silicates which are compounds of oxygen.

• Differences between oxygen and other members of Group VIB.

Oxygen is the first member of Group VIB in the periodic table. The properties of oxygen differ from those of the other members of Group VIB in many respects. These differences are due to the following inherent characteristics of oxygen.

(i) *Small size of oxygen atom,* (ii) *higher electronegativity of oxygen,* (iii) *absence of 'd' orbital in the electronic configuration of oxygen atom.*

The main points of differences between oxygen and the other members of the group are given below :

Period	Elements of Gr VIB	Atomic No	Configuration of valence shell
2	Oxygen ${}_{8}O$	8	$2s^2 . 2p^4$
3	Sulphur ${}_{16}S$	16	$3s^2 . 3p^4$
4	Selenium ${}_{34}Se$	34	$4s^2 . 4p^4$
5	Telurium ${}_{52}Te$	52	$5s^2 . 5p^4$

(i) *Physical state* : Oxygen is a gas while other members of the Group VIB are solids.

(ii) *Abundance in nature* : The occurrence of oxygen in nature is maximum. About 46.6% of earth is oxygen.

(iii) *Atomicity* : Oxygen being a gas, is stable as a diatomic molecule. The molecules of the other elements of the group are somewhat complex in nature, e.g., S and Se occur as S_8 and Se_8 molecules at room temperature.

(iv) *Oxidation state* : The oxidation number of oxygen when combines with fluorine to form oxygen difluoride (OF_2) is '+2'. Excepting this case, the oxidation number of oxygen in general is '−2'. In peroxides the oxidation number of oxygen is '−1'. The oxidation number of all other members of Group VIB are found to be both positive and negative, but the majority of them are found in positive oxidation state.

(v) *Maximum covalency* : As '*d*' orbital is not available in oxygen atom (because here $n = 2$ which can have only two orbitals s and p) the maximum covalency exhibited by it is 2, but due to the presence of '*d*' orbital, the other members of the group exhibit a maximum covalency of 6 up to S*e* and 8 up to the rest. This explains why S can form SF_6 but O can form OF_2.

(vi) *Existence of hydrogen bond* : Due to its high electronegativity and small size of its atom, hydrogen bond plays an important role in the properties of the compounds of oxygen. Due to the presence of hydrogen bond among the H_2O molecules, they get associated and as a result the melting and boiling points of H_2O are much higher than those of the hydrides of the other members of the Group VIB, as hydrogen bonds are not formed in their hydrides due to their low electronegativity and comparatively large size of their atoms.

(vii) *Nature of hydrides* : The hydride of oxygen i.e., water is a colourless, odourless and neutral liquid, but the hydrides of the other elements of this group are gases, combustible, poisonous, having bad odour and acidic in nature.

1.1. Preparation of oxygen.

1. Laboratory method :

[A] Principle : In the laboratory, oxygen is prepared by heating a mixture of *potassium chlorate* and *manganese di-oxide*, when potassium chlorate is decomposed to give *potassium chloride* and *oxygen*. Managnese dioxide acts as *positive catalyst* in this decomposition and remains unchanged after the completion of the decomposition.

$$2KClO_3 + [MnO_2] = 2KCl + 3O_2 \uparrow + [MnO_2]$$

[B] Procedure : (i) A mixture of 4 parts by weight of potassium chlorate and one part by weight of manganese di-oxide is taken in a hard glass test tube. (ii) The mouth of the test tube is fitted with a cork through which passes a bent delivery tube. (iii) The hard glass test tube with its contents is clamped with a stand in a horizontal position but slightly inclined towards its mouth. (iv) The mixture inside the tube is kept spreaded to leave passage for the free escape of oxygen. (v) The hard glass test tube is then heated uniformly from its bottom to its mouth. If the evolution of the

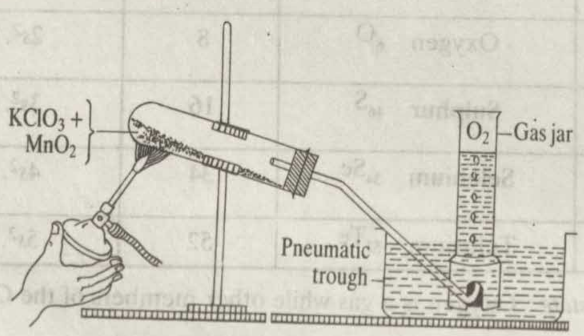


Fig. 1.1 : Preparation of oxygen in the laboratory

gas becomes rapid, the burner may be removed for the time being. (vi) Potassium chlorate decomposes to give off oxygen which passes through the delivery tube. (vii) The air inside the test tube is allowed to escape at first and after its removal, the end of the delivery tube is placed under water through a beehive shelf in a pneumatic trough. (viii) A gas jar full of water is then inverted over the beehive shelf under water and the evolved oxygen is collected in the jar *by the displacement of water*.

[C] Purification : The oxygen thus obtained may contain a slight amount of *chlorine, carbon di-oxide*, and *water vapour* as impurities. The produced oxygen is passed through a concentrated solution of *caustic soda* to remove Cl_2 and CO_2. The gas is then passed through *phosphorus pentoxide* (P_2O_5) to remove water vapour. Pure and dry oxygen is then collected over mercury.

- **Precautions :** The following precautions are to be taken during the preparation of oxygen by the above method.

(i) Potassium chlorate and MnO_2 should be mixed thoroughly and pure MnO_2 freed from carbon and antimony sulphide must be used. MnO_2 contaminated with these impurities may cause explosion during heating. So before using, the purity of the sample should be tested carefully.

(ii) Only half of the hard glass test tube should be filled with the mixture of $KClO_3$ and MnO_2 for the easy escape of the liberated O_2.

(iii) Slow and uniform heating should be applied to avoid rapid evolution of oxygen.

(iv) The mouth of the test tube should be kept along a slightly downward inclination.

(v) After the collection of the gas, the end of the delivery tube should be kept above water to prevent the entry of water in the hot test tube.

• The function of manganese dioxide in the preparation of oxygen from potassium chlorate.

Potassium chlorate when heated alone, decomposes to give off oxygen at high temperature (630°C). The reaction takes place in two steps—

(i) *In the first step,* at about 360°C $KClO_3$ gets melted and decomposes to give a small amount of O_2 and then rapidly converts to *potassium perchlorate* and *potassium chloride*.

$$4KClO_3 = 3KClO_4 + KCl$$

(ii) *In the second step,* at 610°C the residue becomes pasty and at 630°C the produced $KClO_4$ decomposes to give *oxygen* and *potassium chloride*.

$$KClO_4 = KCl + 2O_2$$

If a small amount of MnO_2 is mixed with $KClO_3$ and heated, the decomposition of $KClO_3$ takes place at a lower temperature (200°C — 250°C) and oxygen evolves more rapidly without the formation of $KClO_4$. Thus MnO_2 acts as a positive catalyst and accelerates the decomposition of $KClO_3$ without any change in its mass, composition and chemical properties.

[**Intermediate compound formation theory :** According to Fowler and Grant, MnO_2 may combine with O_2 obtained from $KClO_3$ to form higher oxide of Mn, i.e., Mn_2O_7 which decomposes at a much lower temperature to evolve O_2.

$$\begin{aligned} KClO_3 + 2MnO_2 &= KCl + [Mn_2O_7] \\ [Mn_2O_7] &= 2MnO_2 + 3/2\,O_2\uparrow \end{aligned}$$

That MnO_2 enters into the chemical reaction with $KClO_3$ is also characterised by its change of physical state. It is observed that a lump of MnO_2 is converted to fine powder.

According to Mcleod, MnO_2 probably reacts with $KClO_3$ to form $KMnO_4$ which decomposes at 240°C to give oxygen.

Trace quantity of chlorine is found to be present during this decomposition. This conclusively proves his theory regarding the role of MnO_2 in the decomposition of $KClO_3$.

$$2KClO_3 + 2MnO_2 = 2KMnO_4 + Cl_2 + O_2 \uparrow$$
$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2 \uparrow$$
$$K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2 \uparrow]$$

• The role of MnO_2 as catalyst in the decomposition of $KClO_3$ can be proved by the following experiments.

Experiment : Two hard glass test tubes are taken. In the first one, 5 g of pure $KClO_3$ and in the second one, a mixture of 5 g of $KClO_3$ and 1 g of MnO_2 is taken. The two test-tubes with their contents are now placed vertically side by side in a sand bath. A thermometer is placed vertically on the sand bath near the two test tubes. The sand bath is now heated and when the temperature of the sand bath becomes nearly 250°C, oxygen begins to evolve from the second test tube. When a glowing piece of wood is brought near the mouth of this tube, it bursts into flames. This proves the evolution of O_2 from the second test tube. When the glowing piece of wood is held at the mouth of the first tube, nothing happens. This shows that O_2 has not yet been liberated from the first one. This conclusively proves that $KClO_3$ is decomposed at a lower temperature in presence of MnO_2. Thus MnO_2 accelerates the rate of this reaction acting as a positive catalyst.

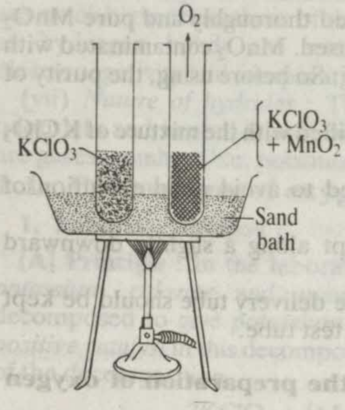


Fig. 1.2 : Action of MnO_2 as positive catalyst

When the evolution of O_2 in the second test tube ceases, the residue is allowed to cool. It is then treated with distilled water when the produced KCl completely dissolves but MnO_2 remains undissolved. It is filtered and the black residue thus obtained is washed with water and then dried in an air oven. After complete drying it is weighed and found that the weight of MnO_2 thus obtained is equal to the weight of MnO_2 originally taken i.e., 1 gram. This proves that the mass of MnO_2 remains unchanged after the completion of the reaction. This MnO_2 can again be used for the decomposition of fresh $KClO_3$. A portion of this residue on being treated with conc. HCl, a greenish yellow gas having the smell of bleaching power is evolved. This proves that the evolved gas is Cl_2 and the black residue is nothing but MnO_2. Thus it is proved that MnO_2 has not undergone any chemical change during this reaction ; it has only accelerated the decomposition of $KClO_3$ simply by its presence only and has played the role of a catalyst in this reaction. Besides manganese dioxide, *cupric oxide, ferric oxide, chromic oxide,* platinum black also act as positive catalyst in the decomposition of potassium chlorate.

1.2. Other methods of preparation of oxygen.

(i) By heating the oxides of weak electropositive metals :

The oxides of weak electropositive metals like Hg, Ag, etc., on being heated strongly, decompose to give off oxygen.

$$2HgO = 2Hg + O_2, \qquad 2Ag_2O = 4Ag + O_2$$

(ii) By heating the nitrates of metals :

(a) *The nitrates of alkali metals like Na, K* etc., on being heated strongly, are decomposed to give the nitrites of the corresponding metals and oxygen.

$$2NaNO_3 = 2NaNO_2 + O_2 \qquad 2KNO_3 = 2KNO_2 + O_2$$

(b) *When the nitrates of heavy metals like Pb, Cu, Fe, Hg* etc., are heated strongly, their corresponding oxides are produced with the evolution of *nitrogen dioxide* and *oxygen.*

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2 \qquad 2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

- **Preparation of oxygen from lead nitrate.**

[A] Principle : Crystals of lead nitrate on being heated strongly, decomposes to give off oxygen and nitrogen dioxide. Lead monoxide is obtained as a yellow residue.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2 \uparrow$$

[B] Procedure : White crystals of lead nitrate are taken in a hard glass test tube. The test tube is fitted with a delivery tube through a cork at its mouth. The other end of the delivery tube is connected to one arm of an empty U-tube kept immersed in a freezing mixture. The other arm of the U-tube is connected to another delivery tube, the free end of which is kept immersed in water in a pneumatic trough. The hard glass test tube is then clamped to a stand and is heated strongly, when lead nitrate decomposes to give off O_2 and NO_2. The mixture of O_2 and NO_2 passes through the U-tube kept in a freezing mixture. Here the brown NO_2 gas gets condensed as a yellow liquid while O_2 passes out through the delivery tube which is collected by the displacement of water.

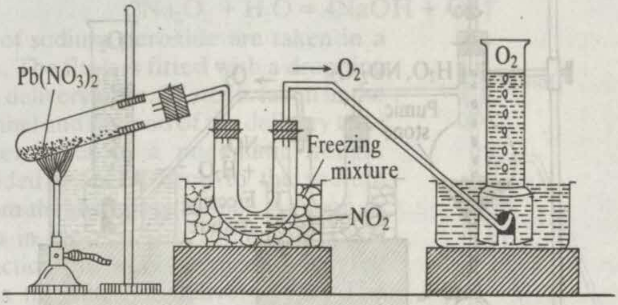


Fig. 1.3 : Preparation of O_2 from lead nitrate

(iii) By the decomposition of compounds rich in oxygen :

Like potassium chlorate, other compounds such as *potassium permanganate* ($KMnO_4$), *potassium dichromate* ($K_2Cr_2O_7$), *red lead* (Pb_3O_4) etc., are rich in oxygen. These compounds on being heated strongly decompose liberating oxygen.

$$2KMnO_4 = \underset{\substack{\text{Potassium}\\\text{manganate}}}{K_2MnO_4} + MnO_2 + O_2$$

$$4K_2Cr_2O_7 = \underset{\substack{\text{Potassium}\\\text{chromate}}}{4K_2CrO_4} + 2Cr_2O_3 + 3O_2$$

$$2Pb_3O_4 = \underset{\substack{\text{Lead}\\\text{monoxide}}}{6PbO} + O_2$$

(iv) By the decomposition of oxyacids :

Oxyacids like *concentrated sulphuric acid* or *nitric acid* when dropped on red hot pumic stone, decompose to give off oxygen.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2\uparrow \;;\; 2H_2SO_4 = 2H_2O + 2SO_2 + O_2\uparrow$$

- **Preparation of oxygen from conc. HNO_3 or conc. H_2SO_4.**

[A] Principle : Conc. HNO_3 on being allowed to fall drop by drop on red hot pumice stone, decomposes to oxygen, nitrogen dioxide and steam.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

[B] Procedure : Some pumice stones are kept inside a distilling flask. A dropping funnel containing conc. HNO_3 is fitted through a cork at its mouth. The side tube of the flask is connected to one arm of an empty U-tube kept immersed in a freezing mixture. The other arm of the U-tube is connected to a delivery tube the end of which is kept under water in a pneumatic trough. The flask is heated strongly and conc. HNO_3 is added drop by drop on the red hot pumice stones. As soon as the concentrated acid comes in contact with the red hot pumice stones, it is thermally decomposed to give off oxygen, nitrogen dioxide and steam. The gas mixture is passed through the U-tube where NO_2 and steam are condensed to give a yellow liquid. Oxygen passes out of the delivery tube and is collected in a gas jar by the displacement of water.

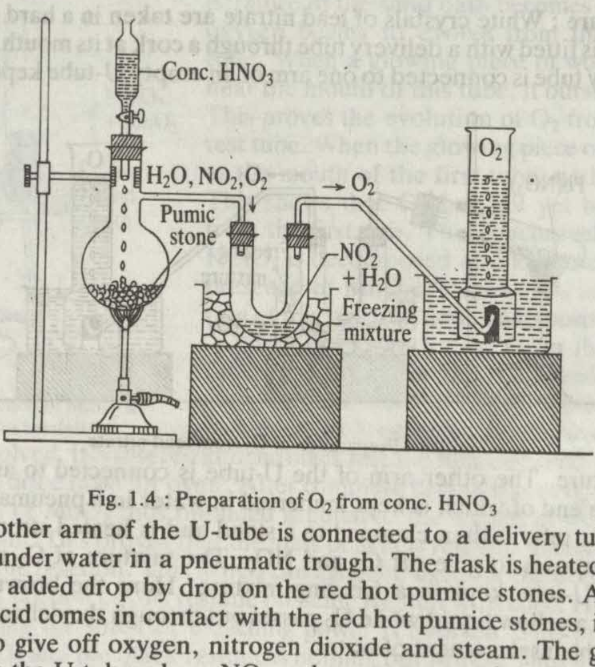


Fig. 1.4 : Preparation of O_2 from conc. HNO_3

Oxygen can also be prepared in a similar way by the thermal decomposition of conc. H_2SO_4 which is thermally decomposed to give oxygen, sulphur dioxide and steam.

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2\uparrow$$

(v) From hydrogen peroxide and peroxide compounds :

(a) When hydrogen peroxide is brought in contact with MnO_2, it decomposes to water and oxygen at ordinary temperature.

$$2H_2O_2 = 2H_2O + O_2$$

(b) When *sodium peroxide* is treated with water at an ordinary temperature it liberates oxygen.

$$2Na_2O_2 + H_2O = 4NaOH + O_2$$

(c) *Bleaching powder* on being treated with hydrogen peroxide oxygen is evolved.

$$Ca(OCl)Cl + H_2O_2 = CaCl_2 + H_2O + O_2$$

(d) Pure oxygen is liberated when an acidified solution of *potassium permanganate* is treated with *hydrogen peroxide* at room temperature.

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$$

• Preparation of oxygen at room temperature i.e., without the application of heat.

(i) Oxygen is prepared in the laboratory *at room temperature* by the action of *water* on *sodium peroxide*. Sodium peroxide reacts with H_2O to liberate O_2. Sodium hydroxide is left as residue.

$$2Na_2O_2 + H_2O = 4NaOH + O_2\uparrow$$

Globules of sodium peroxide are taken in a conical flask. The flask is fitted with a dropping funnel and a delivery tube. Water is taken in the dropping funnel and the end of the delivery tube is kept under water in a pneumatic trough. Water is added drop by drop to the sodium peroxide from the dropping funnel. As soon as water comes in contact with sodium peroxide vigorous reaction starts and oxygen is liberated which passes through the delivery tube. The evolved oxygen is collected in a gas jar by the displacement of water.

(ii) Oxygen may also be prepared *at room temperature without the application of heat* by dropping *hydrogen peroxide* to an *acidified* solution of *potassium permanganate*.

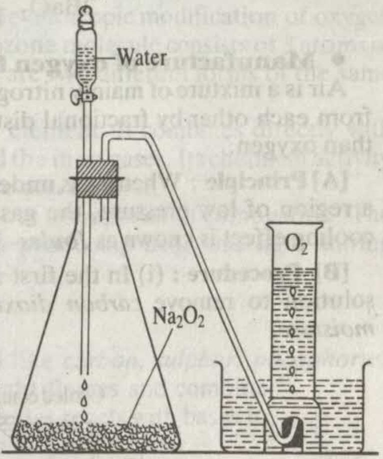


Fig 1.5: Preparation of O_2 at room temperature

$$\begin{array}{llllll}
2KMnO_4 & & = K_2O & + 2MnO & + 5O \\
5H_2O_2 & + 5O & = 5H_2O & + 5O_2 & \\
K_2O & + H_2SO_4 & = K_2SO_4 & + H_2O & \\
2MnO & + 2H_2SO_4 & = 2MnSO_4 & + 2H_2O & \\
\hline
2KMnO_4 & + 5H_2O_2 \quad + 3H_2SO_4 & = K_2SO_4 & + 2MnSO_4 & + 5O_2 + 8H_2O
\end{array}$$

Potassium permanganate solution, acidified with dilute sulphuric acid is taken in a conical flask fitted with a dropping funnel and delivery tube. Hydrogen peroxide taken in the dropping funnel is added drop by drop to the acidified $KMnO_4$ solution. As soon as H_2O_2 comes in contact with the acidified solution of $KMnO_4$, a rapid evolution of oxygen starts. The evolved oxygen is collected in a gas jar by the displacement of water.

(vi) Oxygen from water :

(a) By the electrolysis of water :

A dilute solution of an alkali in water when electrolysed between iron or nickel electrodes, oxygen is liberated at the anode.

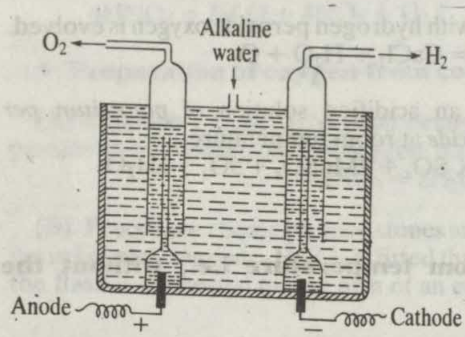


Fig. 1.6 : Preparation of O_2 by the electrolysis of water

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : $2H^+ + 2e = H_2$;

At anode : $2OH^- - 2e = 2OH$

$$4OH = 2H_2O + O_2 \uparrow$$

(vii) Oxygen from air :

(a) **Brin's process :** In this process *barium oxide* is heated in air *under high pressure* at 500°C, when barium oxide absorbs O_2 from air forming *barium peroxide.*

$$2BaO + O_2 = 2BaO_2$$

The produced *barium peroxide on being heated to 800°C* under low pressure, decomposes to give off oxygen.

$$2BaO_2 \xrightarrow[\text{low pressure}]{800°C} 2BaO + O_2$$

- **Manufacture of oxygen from air (Linde's process) :**

Air is a mixture of mainly nitrogen and oxygen. These two gases can be separated from each other by fractional distillation of liquid air, as nitrogen is more volatile than oxygen.

[A] Principle : When a gas under a high pressure is allowed to expand suddenly to a region of low pressure, the gas coming out, suffers a fall of temperature. This cooling effect is known as *Joules- Thomson effect.*

[B] Procedure : (i) In the first step, dust free air is passed through *caustic soda* solution to remove *carbon dioxide* and then through conc. H_2SO_4 to remove *moisture.*

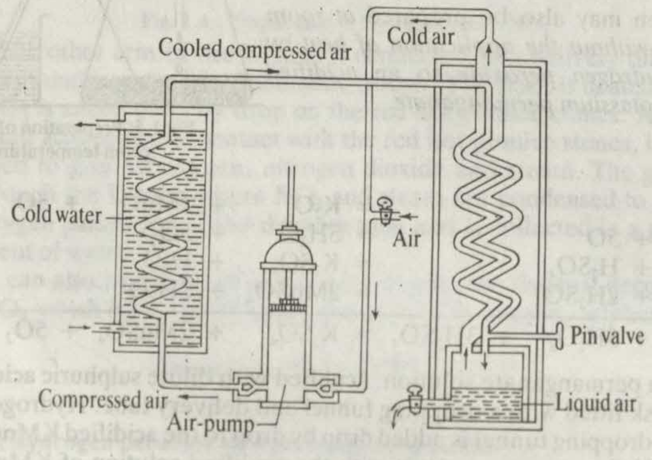


Fig. 1.7 : Preparation of O_2 from liquid air

(ii) The air thus freed from CO_2 and moisture, is then brought under high pressure and the compressed air is cooled by spraying water.

(iii) This air under high pressure is then allowed to expand through a narrow nozzle. Thus the air under high pressure is allowed to expand suddenly to a low pressure. The air coming out through the nozzle suffers a fall of temperature (Joule and Thomson effect).

(iv) The cycle of compression and expansion of air is repeated several times when the temperature of the expanding air finally falls down to −190°C. At this temperature the air is condensed to liquid.

(v) This liquid air is mainly a mixture of liquid oxygen and nitrogen. The boiling point of nitrogen is −190°C and that of oxygen is −183°C. On fractional distillation of this liquid air the more volatile nitrogen evaporates out at first. All the nitrogen being thus removed, almost pure oxygen remains in the distilling vessel as residue. The liquid oxygen thus obtained is stored in steel cylinders.

1.3. Properties of oxygen.

[A] Physical properties : (i) Oxygen is a colourless, odourless, tasteless, neutral gas. (ii) It is little heavier than air. (iii) It is slightly soluble in water (about 4% by volume at 0°C). The dissolved oxygen in water supports the respiration of aquatic animals. (iv) The freezing point of O_2 is −218°C and the boiling point = −183°C. (v) Oxygen is a supporter of respiration. (vi) Oxygen molecule is paramagnetic.

[B] Chemical properties :

1. *Allotropy* : Oxygen exhibits allotropy. The allotropic modification of oxygen is ozone (O_3). Gaseous oxygen is diatomic but ozone molecule consists of 3 atoms of oxygen. As a matter of fact, oxygen and ozone are two different forms of the same element.

2. *Chemical activity* : Oxygen is very active element. It combines directly with most of the elements excepting the halogens and the inert gases. Its chemical activity is enhanced at high temperature and in presence of a catalyst.

3. *Combustion* : Oxygen is not combustible but a supporter of combustion. The combustible substance is oxidised by oxygen producing heat and light during combustion.

4. *Formation of oxides* :

(a) *Reaction with non metals :*

(i) *Formation of acidic oxides :* Non metals like *carbon, sulphur, phosphorus,* etc., on being ignited in oxygen burn with bright flames and combine with O_2 producing *acidic oxides.* This class of oxides reacts with bases to form salts and water and produces acids when dissolved in water.

$C + O_2 = CO_2$, $CO_2 + H_2O = H_2CO_3$ (Carbonic acid)
$S + O_2 = SO_2$, $SO_2 + H_2O = H_2SO_3$ (Sulphurous acid)
$4P + 5O_2 = 2P_2O_5$, $P_2O_5 + 3H_2O = 2H_3PO_4$ (Phosphoric acid)

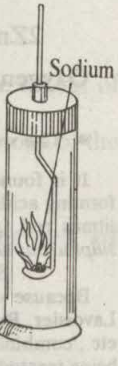


Fig. 1.8

(ii) *Formation of neutral oxides :*

Hydrogen burns in oxygen with a blue flame to form *water* which is a *neutral oxide.*

$$2H_2 + O_2 = 2H_2O$$

Nitrogen combines with oxygen at 3000°C in presence of electric spark forming *nitric oxide* which is also a neutral oxide. This class of oxides does not react with acid or base.

$$N_2 + O_2 = 2NO$$

Oxygen does not combine directly with *chlorine, bromine* or *iodine.*

(b) *Reaction with metals :*

(i) *Formation of basic oxides :* The *alkali metals* such as *sodium, potassium,* etc., and the *alkaline earth metals* such as *calcium, strontium,* etc., combine with oxygen directly producing basic oxides. This class of oxides reacts with acids to form salt and water.

Heated sodium burns in oxygen with a golden yellow flame to form *sodium monoxide*, with excess of oxygen *sodium peroxide* is produced. Sodium monoxide dissolves in water to produce sodium hydroxide—a strong alkali.

$$4Na + O_2 = 2Na_2O, \quad 2Na_2O + H_2O = 2NaOH \text{ (Sodium hydroxide)}$$

$$2Na + O_2 = Na_2O_2 \text{ (Sodium peroxide)}$$

Potassium burns with a violet flame to form *potassium monoxide*, with excess of O_2 *potassium peroxide* is produced.

$$4K + O_2 = 2K_2O, \quad 2K_2O + H_2O = 2KOH$$

$$2K + O_2 = K_2O_2$$

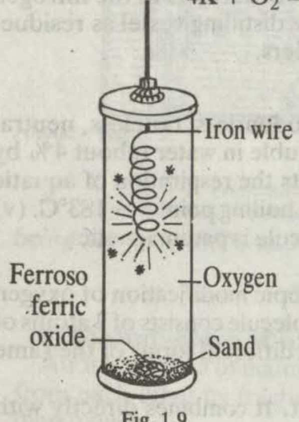


Fig. 1.9

Calcium burns in oxygen with a brick red flame producing *calcium oxide* which is strongly basic.

$$2Ca + O_2 = 2CaO, \quad CaO + H_2O = Ca(OH)_2$$

Magnesium burns in oxygen with a dazzling flame and magnesium oxide is produced. This oxide is feebly basic.

$$2Mg + O_2 = 2MgO$$

Red hot iron on being introduced into a jar of oxygen burns brightly and combines with oxygen to form *ferroso ferric oxide.*

$$3Fe + 2O_2 = Fe_3O_4$$

Weak electro-positive metals like copper, silver etc., on being heated in oxygen are gradually converted to their oxides.

$$2Cu + O_2 = 2CuO, \quad 4Ag + O_2 = 2Ag_2O$$

(ii) *Formation of amphoteric oxide :*

Metals like *aluminium, zinc, tin, lead* produce *amphoteric oxides.* When these metals are heated in oxygen their corresponding oxides are formed which are amphoteric in nature. This class of oxides reacts both with the acids as well as with the alkalis to form salts are water.

$$4Al + 3O_2 = 2Al_2O_3 \left\{\begin{aligned} &Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O \\ &Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O \end{aligned}\right.$$

$$2Zn + O_2 = 2ZnO \left\{\begin{aligned} &ZnO + 2HCl = ZnCl_2 + H_2O \\ &ZnO + 2NaOH = Na_2ZnO_2 + H_2O \end{aligned}\right.$$

Oxygen cannot combine directly with platinum, gold, etc., to form their oxides.

- **The word 'oxygen' means an acid producer, but in some cases the name is misnomer.**

It is found that non-metals like *carbon, sulphur, phosphorus* etc., combine directly with oxygen forming acidic oxides. This class of oxides on being dissolved in water produces acids which turn blue litmus red. As for examples, sulphur burns in oxygen producing *sulphur dioxide* which produces *sulphurous acid* when it is treated with water.

$$S + O_2 = SO_2 ; \quad SO_2 + H_2O = H_2SO_3 \text{ (Sulphurous acid)}$$

Because of such *acid producing* property, oxygen gas was named *'oxygen'* (acid producer) by Lavoisier. But the use of this name is not justified in all cases. Metals like *sodium, potassium, calcium,* etc., combine with oxygen directly producing oxides which are *basic in nature.* This class of oxides on being treated with water produces *alkalis* which turns red litmus blue. These oxides react with acids to form salts and water.

$$4Na + O_2 = 2NaO_2 ; \quad Na_2O + H_2O = 2NaOH$$

Again *hydrogen* burns in oxygen producing water which is neither acidic nor basic in nature. Water is a neutral oxide. Thus in these cases it is found that the name 'acid producer' is not justified—a misnomer one.

5. *Oxidising property :* Oxygen is a strong oxidising agent. It oxidises a substance by combining directly with it or by increasing the proportion of electronegative element in the substance.

(i) *Colourless nitric oxide* gas when comes in contact with oxygen, is oxidised to give brown fumes of *nitrogen dioxide.*

$$2NO + O_2 = 2NO_2$$

(ii) *Sulphurous acid* is oxidised to *sulphuric acid.*

$$2H_2SO_3 + O_2 = 2H_2SO_4$$

(iii) Acidified solutions of *ferrous, stannous* and *cuprous salts* are oxidised to give *ferric, stannic* and *cupric salts* respectively.

$$4\overset{+2}{Fe}SO_4 + 2H_2SO_4 + O_2 = 2\overset{+3}{Fe}_2(SO_4)_3 + 2H_2O$$

$$4\overset{+2}{Fe}Cl_2 + 4HCl + O_2 = 4\overset{+3}{Fe}Cl_3 + 2H_2O$$

$$2\overset{+2}{Sn}Cl_2 + 4HCl + O_2 = 2\overset{+4}{Sn}Cl_4 + 2H_2O$$

$$2\overset{+1}{Cu}_2Cl_2 + 4HCl + O_2 = 4\overset{+2}{Cu}Cl_2 + 2H_2O$$

(iv) In some reactions the oxidising power of oxygen is enhanced in presence of *catalysts.*

(a) At 450°C in presence of *platinum asbestos* or *vanadium pentoxide,* sulphur dioxide is oxidised by oxygen to *sulphur trioxide.*

$$2SO_2 + O_2 \xrightarrow[\text{Pt catalyst}]{450^\circ C} 2SO_3 + \text{Heat.}$$

(b) *Ammonia* is oxidised to *nitric oxide* at 750°C in presence of *platinum* catalyst.

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

- **The reducing action of oxygen :**

Fluorine reacts with oxygen to form oxygen difluoride. $2F_2+O_2=2OF_2$.

As fluorine is more electronegative than oxygen, in this reaction, electrons are accepted by fluorine atom from oxygen atom. Thus fluorine is reduced by accepting electrons from oxygen and on the other hand oxygen is oxidised by donating electrons to fluorine atoms. Thus oxygen is oxidised by fluorine.

$$2F + 2e \rightarrow 2F^- \text{ (Reduction)} \quad O - 2e \rightarrow O^{++} \text{ (Oxidation)} \quad O^{++} + 2F^- \rightarrow OF_2$$

6. *Absorption of oxygen :*

(i) Alkaline solution of *potassium pyrogallate* absorbs oxygen and the colour of the solution *turns brown.*

(ii) Ammoniacal *cuprous chloride* solution absorbs oxygen and the colour of the solution *turns blue.*

1.4. Experiments to illustrate some important properties of oxygen.

(1) Oxygen is a supporter of combustion but it is not combustible.

A glowing piece of charcoal is introduced into a jar full of oxygen. The glowing piece of charcoal at once bursts into flame and burns with a bright flame, but oxygen gas itself does not burn. This proves that oxygen itself is not combustible but is a supporter of combustion.

(2) Oxygen produces acids :

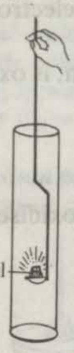


Fig 1.10 :

(a) A piece of charcoal is taken in a deflagrating spoon and held over a bunsen flame till it glows. This glowing charcoal is then introduced into a gas jar full of oxygen. The glowing charcoal immediately bursts into flames and burns vigorously. After the completion of the reaction the spoon being removed, some lime water is added into the gas jar when it turns milky. Thus it is proved that during combustion, charcoal combines with oxygen to form carbon dioxide.

$$C + O_2 = CO_2$$

In another gas jar CO_2 is produced similarly and some water is added into the gas jar. The jar is then shaken well. Now, blue litmus solution is added to the solution in the gas jar, when it turns red showing that the aqueous solution of CO_2 is acidic. Thus it is proved that carbon burns in O_2 forming an acidic oxide CO_2 which when dissolves in water produces carbonic acid.

$$CO_2 + H_2O = H_2CO_3$$

Thus it is proved that O_2 is an acid producer.

(3) Oxygen produces bases :

A piece of sodium is taken in a deflagrating spoon and ignited in bunsen flame. The burning sodium is then inserted into a gas jar full of oxygen. The piece of sodium burns in oxygen producing a golden yellow flame. The residue left after the completion of the reaction is treated with water. To this aqueous solution, red litmus solution is added. The solution turns blue. This proves that sodium reacts with oxygen forming a basic oxide (Na_2O) which on being dissolved in water produces an alkali which turns red litmus blue. Thus it is proved that oxygen is also producer of base.

$$4Na + O_2 = 2Na_2O \qquad Na_2O + H_2O = 2NaOH.$$

(4) The oxidising property of oxygen :

(i) Some copper turnings are taken in a test tube and 1:1 nitric acid is added to it when a colourless gas evolves. This colourless gas is led into a jar of oxygen. It is found that as soon as the colourless gas comes in contact with oxygen, it turns brown. Copper turnings react with 1:1 nitric acid to form colourless nitric oxide. When this gas comes in contact with oxygen, it is oxidised to give nitrogen dioxide which is brown.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$2NO + O_2 = 2NO_2$$

(ii) Ferrous sulphate solution is taken in a test tube and some sulphuric acid is added to it when a colourless solution is obtained. Now oxygen gas is passed through this colourless solution when a yellow solution of ferric sulphate is obtained. Here the acidified solution of ferrous sulphate is oxidised by oxygen to give ferric sulphate.

$$4\overset{+2}{Fe}SO_4 + 2H_2SO_4 + O_2 = 2\overset{+3}{Fe}_2(SO_4)_3 + 2H_2O$$

(5) To show that oxygen is absorbed by alkaline pyrogallate solution :

An alkaline pyrogallate solution is taken in a beaker. A dry test tube completely filled with oxygen is inverted into the solution and kept errect. It is found that the alkaline pyrogallate solution gradually rises up into the test tube and finally fills it up completely. The colour of the solution in the test tube turns brown. This proves that oxygen is absorbed by alkaline pyrogallate solution.

- **Tests for oxygen :**

(i) A glowing piece of wood bursts into flame when it is introduced into a jar of oxygen. By this test O_2 may be identified from all other gases other than *nitrous oxide.*

(ii) Colourless nitric oxide gas when comes in contact with oxygen, brown fumes of nitrogen dioxide are produced.

Oxygen may be distinguished from nitrous oxide by this test.

(iii) Oxygen is absorbed by *alkaline pyrogallate* solution turning it brown.

1.5. Uses of Oxygen.

(i) Oxygen is extensively used in welding and cutting metal sheets by oxy-hydrogen or by oxy-acetylene flames.

(ii) Oxygen is used in hospitals for artificial respiration of patients suffering from breathing troubles. In high altitude or in submarine where the supply of oxygen is insufficient, oxygen is used as an aid to breathing.

(iii) Rockets and jets are driven by a mixture of fuel and liquid oxygen to secure high speed.

(iv) It is used in the laboratory for the estimation of carbon and hydrogen in hydrocarbons.

(v) Catridges of carbon dust soaked in liquid oxygen are used as substitute for dynamite for blasting in coal mines.

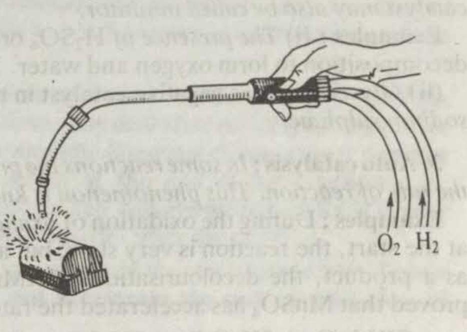


Fig. 1.11 : Oxy-hydrogen flame

(vi) It is also used in the L.D. process for the manufacture of steel. In this process O_2 oxidises the impurites of cast iron.

1.6. Catalyst and Catalysis.

In 1835 *Berzelius* was the first to observe that the rate of many chemical reactions is increased by the presence of a foreign substance, other than the reactants, which remained chemically unchanged after the end of the reaction. Substances having such power of influencing the rate of chemical reactions are called *catalysts.*

Definition : *Catalysis is a process in which the rate of a chemical reaction is increased or decreased by the presence of a small amount of a foreign substance which remains unchanged in mass and chemical composition at the conclusion of the reaction. The foreign substance added is known as catalyst.*

1. Positive Catalyst : *A catalyst which increases the rate of a reaction is called positive catalyst and the process is called positive catalysis.*

Examples : (i) In the preparation of oxygen from potassium chlorate, the presence of *manganese dioxide* accelerates the rate of decomposition of potassium chlorate but itself remains unchanged in mass and chemical composition at the end of the reaction. In this reaction MnO_2 acts as a positive catalyst.

$$2KClO_3 + [MnO_2] = 2KCl + 3O_2 + [MnO_2]$$

(ii) *Powdered iron acts* as a positive catalyst in the synthetic preparation of ammonia from N_2 and H_2

$$N_2 + 3H_2 \xrightarrow[\text{Fe powder}]{500°C} 2NH_3 + \text{Heat}$$

(iii) *Activated charcoal acts* as a positive catalyst in the reaction between hydrogen and chlorine to form hydrogen chloride.

$$H_2 + Cl_2 \xrightarrow[\text{activated charcoal}]{} 2HCl$$

(iv) *Finely divided platinum* or *vanadium pentoxide* (V_2O_5) acts as a positive catalyst in the combination of sulphur dioxide and oxygen to produce sulphur trioxide.

$$2SO_2 + O_2 \xrightarrow[\text{Pt catalyst}]{450°C} 2SO_3 + \text{Heat}$$

2. Negative catalyst : *A catalyst which decreases the rate of a chemical reaction is called negative catalyst and the process is called negative catalysis. The negative catalyst may also be called inhibitor.*

Examples : (i) *The presence of* H_2SO_4 or H_3PO_4 in hydrogen peroxide retards its decomposition to form oxygen and water.

(ii) *Glycerol* acts as negative catalyst in the aerial *oxidation of sodium sulphite to sodium sulphate.*

3. Auto catalysis : *In some reactions the product itself acts as a catalyst and increases the rate of reaction. This phenomenon is known as auto catalysis.*

Examples : During the oxidation of *oxalic acid by acidified $KMnO_4$* it is found that at the start, the reaction is very slow, but as soon as *manganous sulphate* is formed as a product, the decolourisation of $KMnO_4$ becomes instantaneous. Thus it is proved that $MnSO_4$ has accelerated the rate of the reaction.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

4. Catalysis by enzymes—organic catalyst :

There are many chemical reactions which are accelerated by nitrogeneous complex organic compounds produced by living cells in a suitable environment. These nitrogeneous complexes are called enzymes. Enzymes are very specific in their action.

Examples : (i) Enzyme *zymase* produced by the *yeast cells* in glucose solution accelerates the decomposition of *glucose* to *ethyl alcohol* and CO_2

$$C_6H_{12}O_6 \xrightarrow[\text{zymase}]{\text{yeast } 30°C} 2C_2H_5OH + 2CO_2$$

(ii) Enzyme *invertase* catalyses the *hydrolysis of sucrose* into glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

(iii) Thus enzyme *urease* catalyses the hydrolysis of *urea*, enzyme *pepsin* and *lipase* catalyse the hydrolysis of *proteins* and *fats* respectively.

- **Homogeneous and heterogeneous catalysis :**

1. Homogeneous catalysis : *A catalytic reaction in which both the catalyst and the reactants are in the same phase, is known as homogeneous catalysis.*

Examples : (i) The combination of *moist SO_2* and *O_2* to produce sulphuric acid in presence of *nitric oxide as catalyst.*

$$2SO_2(g) + O_2(g) + 2H_2O\,(g) \xrightarrow{NO(g)} 2H_2SO_4$$

(ii) The decomposition of *hydrogen peroxide* in presence of *ferric chloride* solution to produce water and O_2.

$$2H_2O_2(aq) \xrightarrow{FeCl_3(aq)} 2H_2O + O_2$$

2. Heterogeneous catalysis : *A catalytic reaction in which the catalyst and the reactants are in different phases, is known as heterogeneous catalysis*

Examples : (i) The combination of *nitrogen* and *hydrogen* in presence of *iron catalyst :*

$$N_2(g) + 3H_2(g) \xrightarrow{\text{Fe powder }(s)} 2NH_3(g)$$

(ii) *Carbon monoxide* combines with *hydrogen* in presence of *zinc oxide* catalyst to form *methyl alcohol.*

$$CO(g) + 2H_2(g) \xrightarrow{ZnO\,(s)} CH_3OH$$

- **Characteristics of catalytic reactions :**

(i) *Generally a catalyst cannot start a chemical reaction*—it can only increase or decrease the rate of a chemical reaction. There are, however, a few reactions where a catalyst appears to start it.

(ii) *A catalyst remains unchanged in mass and chemical composition after the conclusion of the reaction.* There may be some physical changes of a catalyst after the reaction or a catalyst may undergo intermediate chemical changes but it remains unchanged in mass and chemical composition at the end of the reaction e.g., coarsely powdered manganese dioxide used in the decomposition of $KClO_3$ may undergo a physical change to form a very fine powder after the reaction.

(iii) *A very small amount of the catalyst can influence the rate of a reaction.* Thus a very small amount of platinum asbestos can accelerate the rate of oxidation of sulphur dioxide by air.

(iv) *A catalyst cannot influence the equilibrium in a reversible reaction.* The rate of the forward and backward reactions are equally influenced by the catalyst. The catalyst only brings the equilibrium quickly.

(v) *A catalyst is specific in its action.* It is found that a catalyst for a particular reaction fails to catalyse the other reactions. There is no universal catalyst. As for example, iron powder is a catalyst for the combination of N_2 and H_2 only. Finely divided nickel is a catalyst for the hydrogenation reactions.

(vi) *A catalyst has an optimum temperature.* At this temperature the cayalyst becomes most active.

Promoters : In some cases the activity of a catalyst is appreciably increased by the addition of a small amount of the other substance which is not a catalyst and which also remains unchanged in mass and composition at the end of the reaction. This substance is called promoter. *A promoter is a substance which promotes the catalytic action of a catalyst, e.g., molybdenum* or *oxides of potassium or aluminium acts* as a promoter in the combination of N_2 and H_2 to increase the *efficiency of iron catalyst. Chromic oxide* (Cr_2O_3) promotes the activity of *ZnO catalyst* in the combination of CO and H_2. Most probably the fine particles of the promoter are deposited on the surface of the catalyst thereby increasing the number of active centres on the surface of the catalyst which increases the adsorbing capacity of the catalyst. As a result the efficiency of the catalyst increases.

Catalytic poisons : *In some cases, the activity of a catalyst is appreciably decreased or completely destroyed by the presence of traces of some foreign substances along* *with the reactants. Such substances are called catalytic poisons and the phenomenon in known as the poisoning of the catalyst.*

As for example, in contact process, the presence of a trace of arsenious oxide (As_2O_3) in the mixture of SO_2 and air, completely destroys the catalytic power of platinum asbestos in the manufacture of sulphuric acid. Traces of CO poison the iron catalyst in the combination of N_2 and H_2. Poisoning action is also specific. Thus a promoter activates a catalyst where as a catalytic poison destroys the activity of a catalyst.

- **How does a catalyst influence the rate of a chemical reaction ?**

A catalyst may influence the rate of a reaction in one of the following ways—

(i) By the formation of an intermediate compound (In case of homogeneous catalysis) and

(ii) By adsorption (In case of heterogeneous catalysis).

(i) **Intermediate compound formation theory :**

According to this theory, the catalyst first reacts with one of the reactants to form an intermediate compound, which subsequently reacts with the other to yield the final products. The catalyst is regenerated during the second step.

Let us consider the reaction $A + B \rightarrow AB$ in which C is a catalyst.

$A + B \rightarrow AB$. The rate of this reaction is very slow as the energy of activation is very high. The catalyst C at first reacts with A to produce an intermediate compound AC. In the second step AC thus produced reacts with B to form AB and regenerating C. The rate of both the reactions is fast as the energy of activation of both the reaction is low. As both the reactions are fast the formation of the product AB is also fast.

$$\begin{array}{c} A + C = AC \\ AC + B = AB + C \\ \hline A + B + [C] = AB + [C] \end{array}$$

The catalytic oxidation of SO_2 to SO_3 in the *Chamber process* is shown below.

$$\begin{array}{c} O_2 + 2NO = 2NO_2 \\ 2SO_2 + 2NO_2 = 2SO_3 + 2NO \\ \hline 2SO_2 + O_2 + [2NO] = 2SO_3 + [2NO] \end{array}$$

The presence of NO_2 in the reaction chamber proves the validity of this theory.

(ii) **Adsorption theory and energy of activation :**

The activity of a catalyst is not distributed uniformly on the surface of the catalyst, rather it is concentrated at some points on the surface of the catalyst. The points on the surface of a catalyst where the catalytic activity is maximum are known as *active centres*. According to adsorption theory the molecules of the reactants are adsorbed at the active centres on the surface of the catalyst. The forces that hold the atoms in the molecules of the reactants become weak due to this adsorption and as a result the adsorbed molecules become more active than the unadsorbed molecules. Thus due to lower energy of activation the adsorbed molecules form the activated complex more quickly than the unadsorbed ones. The activated complex thus produced, decomposes rapidly to form the product which comes out of the surface of the catalyst and thus the surface becomes free to adsorb more reactants.

The increased concentration of the adsorbed molecules of the reactants on the surface of the catalyst is also responsible for the increased rate of the reaction.

The main function of the catalyst is to offer an alternative lower path with lower activation energy and as a consequence the rate of reaction becomes faster. The following diagram indicates the energy of activation for the catalysed and uncatalysed reactions. [For detail see chemical kinetics chapter Vol. II]

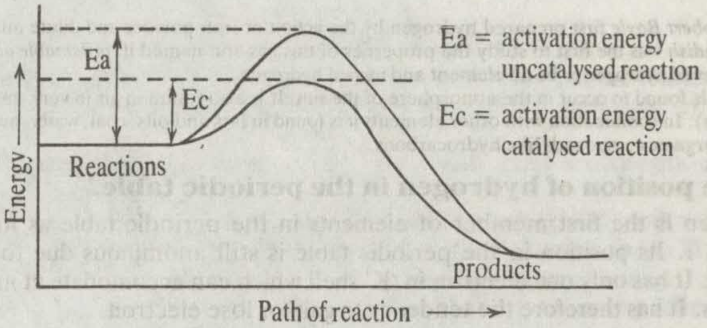


Fig. 1.12

• Applications of catalysis in industry :

Catalytic processes are of great importance in chemical industry. Some of these are given below—

(i) **Manufacture of sulphuric acid :** In the manufacture of sulphuric acid by contact process, *platinised asbestos* or *vanadium pentoxide* is used as a catalyst in the oxidation of sulphur dioxide to sulphur trioxide. SO_2 is oxidised to SO_3 by air in presence of platinised asbestos or vanadium pentoxide as a catalyst at 450°C.

$$2SO_2 + O_2(\text{air}) \xrightarrow{\text{Pt asbestos}} 2SO_3 + \text{heat.}$$

(ii) **In the synthesis of ammonia :** In the manufacture of ammonia by Haber's process *finely divided iron* is used as a catalyst.

(iii) **In the synthesis of hydrogen chloride :** Hydrogen chloride is manufactured by the combination of H_2 and Cl_2 is presence of *active charcoal* as a catalyst.

(iv) **Hydrogenation of oils:** *Finely divided nickel* enhances the addition of hydrogen to unsaturated vegetable oil to convert it into saturated oil which is fat.

(v) **Synthesis of methanol :** Methanol is manufactured from *carbon monoxide* and hydrogen in presence of ZnO as a catalyst and Cr_2O_3 as a promoter at 400°C.

$$CO + 2H_2 = CH_3OH$$

(vi) **Manufacture of nitric acid :** In the manufacture of nitric acid by Ostwald process *platinum wire gauze* is used as a catalyst in the oxidation of ammonia by air.

$$4NH_3 + 5O_2(\text{air}) = 4NO + 6H_2O$$

(vii) **Bosch process :** In the large scale production of hydrogen by Bosch process CO of water gas is oxidised to CO_2 by steam in presence of *Ferric oxide* as catalyst.

$$(CO + H_2) + H_2O = CO_2 + 2H_2$$

• HYDROGEN •

Symbol—H	**Atomic No : 1**	**Atomic wt : 1·008**
Electronic configuration : $1s^1$		**Oxidation Nos : (+1), (−1)**

In 1660 *Robert Boyle* first prepared hydrogen by the action of iron powder and dilute mineral acid. *Henry Cavendish* was the first to study the properties of this gas and named it *'inflamable air'*. In 1783 Lavoisier proved hydrogen to be an element and named hydrogen.

Hydrogen is found to occur in the atmosphere of the sun. It is also found in air in very small amount (about 1 ppm). In combination with other elements it is found in fats and oils, coal, water, acids, alkalis and in most organic compounds like hydrocarbons.

1.7. The position of hydrogen in the periodic table.

Hydrogen is the first member of elements in the periodic table as its atomic number is 1. Its position in the periodic table is still anomarous due to its duel behaviour. It has only one electron in 'K' shell which can accomodate at maximum 2 electrons. It has therefore the tendency to gain or lose electron.

(a) Resemblance with halogens :

(i) **Electronic configuration :** The electronic arrangement of the outermost orbit in halogen atom is expressed by $ns^2.np^5$ i.e., one electron is needed to have the structure of inert gas. The electronic arrangement of hydrogen atom is $1s^1$, i.e., one electron is needed to have the structure of helium atom. Thus, both hydrogen and the halogens behave as monovalent electronegative element in the formation of compounds by gaining one electron.

(ii) **Ionisation potential :** The ionisation potential of hydrogen is 13.5 *ev* and those of halogens are F = 18.6 *ev* ; Cl = 18.0 *ev* ; Br = 16.6 *ev* ; whereas the ionisation patentials of the elements of Group I are much less than that of hydrogen. Thus, it is found that the I. P. of hydrogen is of the same order as those of the halogens.

(iii) **Atomicity :** Like halogen molecules, hydrogen molecule is also diatomic (H_2)

(iv) **Physical state :** Hydrogen like the halogens, is a non-metal and like fluorine and chlorine, hydrogen is also a gaseous element.

(v) **Electronegative character :** Hydrogen and the halogens combine with strong electropositive elements like Li, Na, K etc., forming hydrides and halides respectively.

$$2Na + H_2 = \underset{\text{sodium hydride}}{2NaH} \; ; \qquad 2Na + Cl_2 = \underset{\text{sodium chloride}}{2NaCl}$$

Fused halides on electrolysis liberate halogens at the anode. Similarly the fused hydrides on electrolysis liberate hydrogen at the anode.

$$NaCl = Na^+ + Cl^- \qquad NaH = Na^+ + H^-$$

$$\textit{At anode}: 2Cl^- - 2e = Cl_2\uparrow \qquad \textit{At anode}: 2H^- - 2e = H_2\uparrow$$

(vi) **Formation of covalent compounds :** Carbon, silicon, germanium, etc., form a similar type of covalent compounds with hydrogen and the halogens, e.g., CH_4, CCl_4, SiH_4, $SiCl_4$ etc. These compounds possess similar arrangements of atoms in the molecules.

(vii) *The four hydrogen atoms of methane can be replaced by Cl atoms forming different compounds*

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

This proves the similarity in the behaviour of hydrogen and chlorine atoms.

(b) Resemblance with alkali metals :

(i) Like the alkali metals hydrogen has got one electron in its outermost orbit.

H —$1s^1$
Li —$1s^2.2s^1$
Na —$1s^2.2s^2.2p^6.3s^1$
K —$1s^2.2s^2.2p^6.3s^2.3p^6.4s^1$.

(ii) **Valency :** Like alkali metals the hydrogen atom has got the tendency to lose the single electron in its outermost orbit and thus it exhibits monovalency in forming compounds.

(iii) **Electropositive character :** Like the alkali metals hydrogen is also an electropositive element.

(iv) Like the metallic ions, hydrogen also forms cation (H_3O^+) with water.

(v) When hydrogen halides are dissolved in water they give rise to H^+ ions like alkali halides which produce Na^+, K^+ etc., in their aqueous solution.

(vi) Both the hydrogen and the alkali metals have got a strong affinity for the non-metals and less affinity for the metals.

(vii) The aqueous solution of HCl on electrolysis liberates hydrogen at the cathode just like the alkali metals which are liberated at the cathode when their fused chlorides are electrolysed.

$HCl = H^+ + Cl^-$ $NaCl = Na^+ + Cl^-$
At cathode : $2H^+ + 2e = H_2$ *At cathode* : $Na^+ + e = Na$

- **Special position of hydrogen in the Periodic table :**

(i) The oxide of hydrogen (H_2O) is neutral—it is not acidic like the oxides of halogens (Cl_2O_7) and not basic like those of the alkali metals (Na_2O).

(ii) There is a marked difference in the atomic structure of hydrogen atom (having one proton in the nucleus and one electron in 1*s* orbital) and the other elements.

(iii) Hydrogen resembles carbon in many respects. The outer shells of both hydrogen and carbon atoms are half filled. Hydrogen has got one electron only in its outermost orbit = 1/2 duplet and carbon has got 4 electrons in its outermost orbit = 1/2 octet.

(iv) Both hydrogen and carbon have similar values of electro-negativity. In this respect hydrogen differs from the alkali metals and from the halogens.

Li = 1.0 H = 2.1 F = 4.0
Na = 0.9 C = 2.5 Cl = 3.0

(v) When carbon and hydrogen combine with other elements to form covalent bond, no outer electron is left behind e.g., CCl_4, HCl.

Thus for its similarity to carbon atom in Group IVA, it has been suggested that hydrogen be placed above carbon in a separate independent position in the periodic table, thus a special position was given to hydrogen by Thomson as follows :

	I	II	III	IV	V	VI	VII	O
1				H				He
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar

First three periods of Thomson's periodic table

1.8. Preparation of hydrogen.

1. Laboratory method of preparation :

[A] Principle : Hydrogen is prepared in the laboratory by the action of dilute sulphuric acid on granulated zinc at an ordinary temperature. As a result of the reaction zinc sulphate and hydrogen are produced.

$$Zn + H_2SO_4 = ZnSO_4 + H_2 \uparrow$$

[B] Procedure : (i) Some commercial granulated zinc are taken in a woulfe's bottle fitted with air-tight corks. (ii) Through one of the corks a thistle funnel is inserted into the woulfe's bottle, the lower end of which reaches almost the bottom of the woulfe's bottle. Through the other cork, a delivery tube is inserted into the bottle.

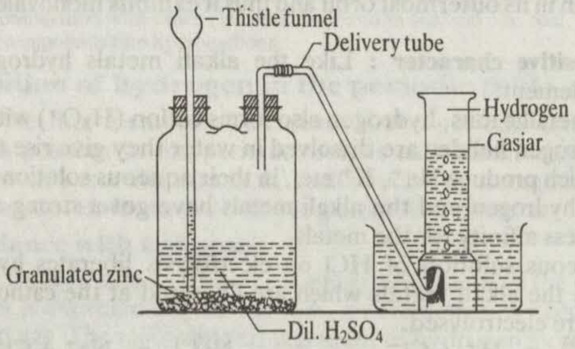


Fig. 1.13 : Preparation of H_2 in the laboratory

(iii) Now water is added into the woulfe's bottle down the thistle funnel so that the end of the thistle funnel and the zinc granules are kept immersed in water. The lower end of the delivery tube should be kept above the water surface. (iv) As the aerial oxygen forms an explosive mixture with hydrogen, the apparatus must be perfectly air-tight. (v) This being done, the end of the delivery tube is kept under water in a bee-hive self in a pneumatic through. (vi) Now dilute sulphuric acid (1 : 4) is added to the zinc granules down the thistle funnel. As soon as the zinc granules come in contact with the acid, the reaction starts and hydrogen begins to evolve. The evolved hydrogen passes through the delivery tube. Some gas is allowed to escape to remove the air inside the woulfe's bottle. (vii) A gas jar completely filled with water is then inverted over the end of the delivery tube under water. Hydrogen is collected in the gas jar by the downward displacement of water.

[C] Purification : Hydrogen gas thus produced contains traces of *hydrogen sulphide* (H_2S), *arsine* (AsH_3), *phosphine* (PH_3), *carbon di-oxide* (CO_2), *sulphur dioxide* (SO_2), *oxides of nitrogen* and *moisture*. The impure hydrogen gas is successively passed through several U tubes. It is first passed through a U tube containing *lead nitrate solution* to remove H_2S, then through *silver nitrate solution* to remove *phosphine* and *arsine*. It is next passed through a concentrated solution of *caustic potash* to remove CO_2, NO_2 and SO_2 and finally through P_2O_5 to remove moisture. After removing all the impurities pure hydrogen is collected over mercury.

$$Pb(NO_3)_2 + H_2S = PbS \downarrow + 2HNO_3$$
$$6AgNO_3 + PH_3 = Ag_3P.3AgNO_3 + 3HNO_3$$
$$6AgNO_3 + AsH_3 = Ag_3As.3AgNO_3 + 3HNO_3$$
$$2KOH + CO_2 = K_2CO_3 + H_2O$$
$$2KOH + SO_2 = K_2SO_3 + H_2O$$
$$2KOH + 2NO_2 = KNO_3 + KNO_2 + H_2O$$

A trace of N_2 remains in the hydrogen thus obtained. To remove N_2, the hydrogen is passed through a glass bulb containing palladium plates. H_2 is adsorbed by palladium and the unadsorbed N_2 is pumped out. When the bulb is heated, pure H_2 freed from N_2 is liberated from palladium.

- **Precautions to be taken in the preparation of hydrogen :**

The following precautions are to be taken during the preparation of H_2 in the laboratory.

(i) The end of the thistle funnel and zinc granules in the woulfe's bottle must be kept immersed in the acid solution.

(ii) Before the collection of the gas, it is allowed to escape for some time, so that the air inside the woulfe's bottle is completely removed.

(iii) The gas jars used for the collection of H_2 must be filled with water completely and there should be no air bubble inside the gas jars.

(iv) The whole apparatus must be perfectly air tight. To test for this, air is forced into the woulfe's bottle through the open-end of the delivery tube when water inside the bottle rises up the stem of the thistle funnel. The end of the delivery tube is then closed by pressing finger on it. If the whole apparatus is completely air tight, the water column in the stem of the thistle funnel will not come down but will remain fixed.

(v) Violent explosion takes place when a mixture of hydrogen and oxygen comes in contact with flame. So no flame should be kept nearby the apparatus.

- **Conc. H_2SO_4 or conc. HCl or HNO_3 is not used in the preparation of hydrogen :**

(i) **Conc. H_2SO_4 :** Hydrogen gas cannot be prepared by the action of conc. H_2SO_4, on metallic zinc because due to the acidic property of conc. H_2SO_4, hydrogen is replaced by the metal from H_2SO_4, but due to its oxidising property, the nascent oxygen evolved by the decomposition of conc. H_2SO_4 oxidises the evolved H_2 to form water.

$$\begin{gathered}H_2SO_4 + Zn = ZnSO_4 + H_2\\ H_2SO_4 = H_2O + SO_2 + O\\ H_2 + O = H_2O\\ \hline 2H_2SO_4 + Zn = 2H_2O + SO_2 + ZnSO_4\end{gathered}$$

(ii) **Conc. HCl :** It is a non oxidising acid and so it can evolve H_2 by its action on metallic zinc. But as conc. HCl is very volatile, the produced H_2 will get contaminated with HCl vapour. So concentrated hydrochloric acid is not found to be fit to prepare H_2 by its action on metallic zinc.

(iii) **Nitric acid :** Due to the acid property of nitric acid, its hydrogen is replaced by metallic zinc, but due to its oxidising action, the nascent oxygen evolved by its decomposition, oxidises the evolved H_2 to produce water. Thus hydrogen is not obtained by the action of zinc on HNO_3. *Magenesium and manganese are the only metals which liberate hydrogen from dilute nitric acid.*

$$\begin{gathered}2HNO_3 + Zn = Zn(NO_3)_2 + 2H\\ 2HNO_3 = H_2O + 2NO_2 + O\\ H_2 + O = H_2O\\ \hline 4HNO_3 + Zn = Zn(NO_3)_2 + 2NO_2 + 2H_2O\end{gathered}$$

- **Pure zinc is not used in the preparation of hydrogen—Explain why ?**

When pure zinc and dilute sulphuric acid react together, hydrogen evolves very slowly and a thin film of H_2 gas is formed on the surface of pure zinc. Thus very soon the acid cannot come in contact with the metallic zinc and as a result the reaction stops. But if impure commercial zinc is used, this layer of hydrogen cannot be formed on the surface of zinc. As a result, the acid can react with zinc fully and hydrogen is produced without any disturbance. In fact, small cells are produced by zinc and the impurities present in commercial zinc, consequently the rate of reaction between zinc and the acid is increased. For this reason a little $CuSO_4$ solution is added to dilute H_2SO_4 to increase the rate of the reaction.

- **Moist hydrogen is not dried by passing it through con. H_2SO_4—Explain why ?**

Hydrogen is a good reducing agent. On the other hand conc. H_2SO_4 is an oxidising agent. Consequently hydrogen reduces conc. H_2SO_4 to SO_2 while passing through it. For this reason, moist H_2 is not dried by conc. H_2SO_4.

$$\begin{array}{c} H_2SO_4 = H_2O + SO_2 + O \\ H_2 + O = H_2O \\ \hline H_2SO_4 + H_2 = 2H_2O + SO_2 \end{array}$$

1.9. Hydrogen produced in Kipp's apparatus :

Kipp's apparatus is conveniently used for getting a ready and continuous supply of hydrogen gas in the laboratory. Kipp's apparatus consists of two parts. The lower part of the apparatus is the combination of two globes—one full and other half-joined together by a narrow neck. The upper globe is provided with an exit tube with a stop cock. The exit tube is fitted with this globe by means of a rubber cork. The lower globe has an outlet to remove zinc sulphate produced by the reaction in it. The upper part of the apparatus is another globe which is provided with a long stem which fits air tight into the neck of the middle globe. The stem of the upper globe reaches the bottom of the lower half-globe. Granulated zinc is introduced into the middle globe. The stop cock is opened and dilute sulphuric acid is added into the apparatus through a funnel. It fills the bottom globe and then comes in contact with the zinc granules in the central globe. As soon as the zinc granules come in contact with the acid, reaction takes place and hydrogen is evolved which passes out of the exit tube.

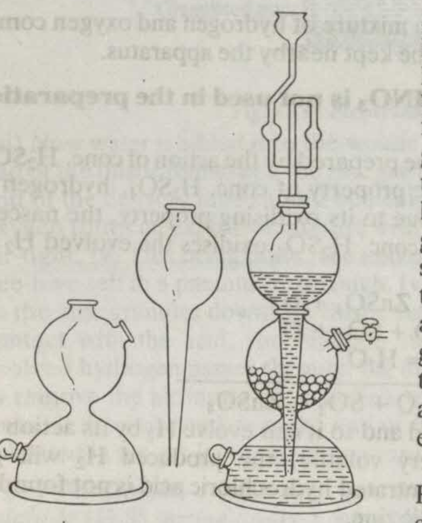


Fig. 1.14 : Kipp's apparatus

The stop cock is closed and so the evolved H_2 gas cannot get out of the globe and so it exerts pressure on the acid level and forces it to go down into the lower globe. Thus the contact between Zn and H_2SO_4 is stopped and as a result the reaction stops. So the evolution of H_2 is stopped also.

When the gas is needed, the stop cock is opened and the evolved gas, stored in the mid-globe, escapes through the outlet. Thus the pressure inside the globe falls and so acid level rises up again and comes in contact with zinc and the gas evolves again.

1.10. Other methods of preparation of hydrogen.

1. From acids : The metals which are more electro-positive than hydrogen (Mg, Al, Zn, Fe, Sn etc.), react with dil. H_2SO_4 or HCl producing salts and liberating hydrogen. Thus magnesium, aluminium, zinc, iron etc., react with dil. H_2SO_4 or HCl producing their corresponding salts and hydrogen.

$$Mg + H_2SO_4 = MgSO_4 + H_2, \quad 2Al + 6HCl = 2AlCl_3 + 3H_2$$
$$Fe + H_2SO_4 = FeSO_4 + H_2, \quad Zn + 2HCl = ZnCl_2 + H_2$$

[Sodium and potassium should not be used to prepare H_2 from HCl or dil. H_2SO_4 as the reactions are vigorous and explosion may take place]

N.B. : The metals which are above hydrogen in the electro-chemical series can replace H_2 from dil. H_2SO_4 or HCl. Metals which are below hydrogen i.e., less electro-positive than hydrogen, cannot replace H_2 from dil. H_2SO_4 or HCl. According to the electronic theory of oxidation and reduction, an element whose standard reduction potential is less than that of hydrogen, can reduce H^+ ion to H_2 gas. The standard reduction potential of elements is expressed by the symbol E^0.

$$E^0_{2H^+/H_2} = 0 \text{ volt}, \quad E^0_{Zn^{++}/Zn} = -0.76 \text{ volt}, \quad E^0_{Ag^+/Ag} = +0.8 \text{ volt}.$$

As the value of $E^0_{2H^+/H_2} = 0$ volt, is greater than $E^0_{Zn^{++}/Zn}$, zinc has got the power to reduce H^+ ions to H_2 gas.

$$Zn + 2H^+ = Zn^{++} + H_2 \uparrow$$

On the other hand the value of $E^0_{Ag^+/Ag}$ is greater than the value of $E^0_{2H^+/H_2}$, and so Ag cannot reduce H^+ ions to H_2, i.e., cannot replace hydrogen from dil. H_2SO_4 or HCl.

2. From alkalis : Hydrogen may also be produced by the action of powdered metals like *aluminium, zinc* and non metals like *silicon* on hot and concentrated solution of strong alkali like *caustic soda* or *caustic potash*.

$$2NaOH + Zn = Na_2ZnO_2 + H_2,$$
$$2NaOH + Si + H_2O = Na_2SiO_3 + 2H_2$$
$$2NaOH + 2Al + 2H_2O = 2NaAlO_2 + 3H_2$$

3. From water : Water is the cheapest and abundant source of hydrogen.

(i) *By the electrolysis of water :* When a 20% solution of sodium hydroxide is electrolysed using iron as cathode and nickel plate as anode, hydrogen is liberated at the cathode.

$$H_2O \rightleftharpoons H^+ + OH^-, \qquad \textit{At cathode} : 2H^+ + 2e = H_2$$

(ii) *By the action of metals on water at ordinary temperature :*

Strong electro-positive metals like *potassium, sodium, calcium,* etc., react with water at ordinary temperature to form their respective hydroxides with the evolution of hydrogen.

$$2K + 2H_2O = 2KOH + H_2 \; ; \quad 2Na + 2H_2O = 2NaOH + H_2$$
$$Ca + 2H_2O = Ca(OH)_2 + H_2$$

Sodium and *potassium* react with *water* so vigorously that very often explosions take place. To control the reaction, their *amalgams* are used in place of the metals, e.g., sodium amalgam reacts with water less vigorously at ordinary temperature liberating hydrogen.

Some metals cannot decompose water ordinarily but do so in *the form of couple.* For examples aluminium mercury couple and zinc copper couple liberate hydrogen when they come in contact with water.

(iii) *By the action of metals on boiling water :*

Metals like *Aluminium, Magnesium* etc., react with boiling water liberating hydrogen and forming their corresponding hydroxides e.g., aluminium powder on being treated with boiling water liberates hydrogen with the formation of aluminium hydroxide.

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2, \qquad Mg + 2H_2O = Mg(OH)_2 + H_2$$

(iv) *By the action of red hot metals on steam :*

Red hot *iron* or *zinc* or *magnesium* decomposes superheated steam with the evolution of hydrogen. Thus when super heated steam is passed over red hot iron or zinc, hydrogen is evolved and the corresponding oxides are produced.

$$\underset{\text{red hot}}{3Fe} + \underset{\text{steam}}{4H_2O} = \underset{\substack{\text{Ferrosoferric}\\ \text{oxide}}}{Fe_3O_4} + 4H_2$$

$$Zn + H_2O = ZnO + H_2$$

4. Hydrolith process : Hydrogen is liberated by the action of metallic hydrides on water.

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2\uparrow, \quad NaH + H_2O = NaOH + H_2$$

5. Preparation of pure hydrogen : A warm solution of *barium hydroxide* is electrolysed in a U-tube *using platinum electrodes.* During the electrolysis, water

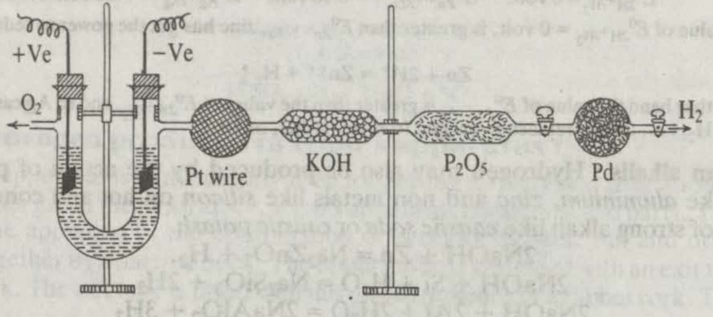


Fig. 1.15 : Preparation of pure H_2

decomposes yielding H_2 *at the cathode* and O_2 *at the anode.* Here the function of $Ba(OH)_2$ is only to make water a conductor of electricity, as pure water is not a good conductor.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode : $2H^+ + 2e = H_2\uparrow$ *At anode* : $2OH^- - 2e = 2OH$

$$4OH = 2H_2O + O_2\uparrow$$

The hydrogen thus produced is passed over heated *platinum gauze* when any O_2 present, is converted to H_2O. The gas is then passed through solid *caustic soda* and *phosphorus pentoxide,* when it is dried and made free from other impurities. The dry gas is adsorbed in palladium which when heated under reduced pressure yields pure hydrogen.

1.11. Large scale preparation of hydrogen.

1. Hydrogen by the action of steam on red hot iron—Lane's process :

[A] Principle : When steam is passed over red hot iron, steam is decomposed to give off hydrogen with the formation of *ferrosoferric oxide.*

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 + \text{Heat.}$$

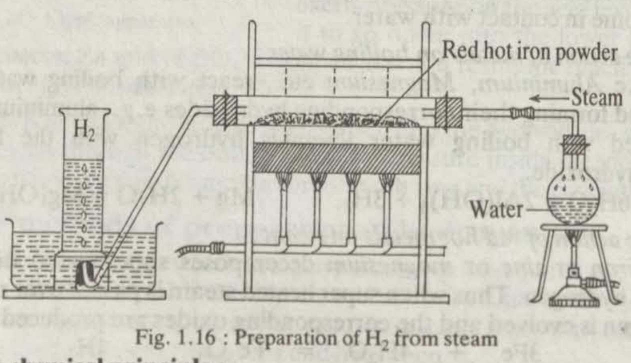


Fig. 1.16 : Preparation of H_2 from steam

[B] Physico chemical principle :

The reaction is (i) *reversible,* (ii) *the forward reaction is exothermic,* (iii) *the number of moles of the reactant gas (steam) is equal to that of the product (H_2).*

(a) **Effect of temperature :** As the forward reaction is exothermic the backward reaction is endothermic. So according to Le Chatelier's principle, if the reaction is carried out at high temperature the reaction will take place in such a direction so that the excess heat may be neutralised. As the backward reaction is endothermic, the backward reaction will take place and so the yield of H_2 will decrease with the rise of temperature.

If the reaction is carried out at low temperature, the forward reaction will take place. But at the low temperature the rate of the reaction becomes very slow. It has been observed that if the reaction is carried out at 750°C, the rate of the reaction as well as the yield of hydrogen become satisfactory. Thus the *optimum temperature* for this reaction is 750°C.

(b) **Effect of pressure :** As the number of moles of steam (reactant) and hydrogen (product) are the same, pressure has no effect on the yield of hydrogen. Consequently the reaction is carried out at ordinary pressure.

(c) **Concentration of the reactants :** The equilibrium constant K_p for this reaction is expressed as $K_p = \frac{(P_{H_2})^4}{(P_{H_2O})^4}$ (Fe and Fe_3O_4 are not considered here as they are solids). It is observed that if the concentration of steam is increased, the forward reaction will be favoured and consequently the yield of H_2 will increase. So excess of steam is used in this reaction.

[C] Procedure : Several retorts are packed with iron powder and kept in vertical position. The iron in the retorts are made red hot by heating them at 750°C in a furnace. Now steam is passed over the red hot iron when it is decomposed to give off hydrogen and iron is oxidised to produce ferrosoferric oxide. The produced hydrogen is passed through an outlet tube and is collected in gas holders by the downward displacement of water.

[D] Regeneration of iron : Iron is regenerated by reducing the produced ferrosoferric oxide by water gas [$CO + H_2$] and is used again.

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$
$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$$

In practice, the steam is passed over the red hot iron for *10 minutes* and this period is known as *oxidation* or *gas period*. After this, water gas ($CO + H_2$) is blown through the heated ferrosoferric oxide for *20 minutes*. This period is known as *reduction period*.

Both the oxidation and the reduction periods are carried out alternatively by using two or more furnaces to make the whole process continuous. The hydrogen obtained by this process is about 98.5—99% pure.

2. Hydrogen from water gas—Bosch process :

A large amount of hydrogen is manufactured from water gas. The process consists of the following steps :—

(i) **Preparation of water gas :** Steam is passed over white hot coke kept at 1400°C when coke is oxidised by steam to produce *equal volumes of carbon monoxide* and *hydrogen. The mixture of these two gases in equal volumes is known as water gas.*

$$C + H_2O = CO + H_2$$

Carbon dioxide is produced instead of CO if the temperature is decreased.

(ii) **Removal of CO from water gas :** The carbon monoxide present in water gas is removed by the following process—

(a) *Conversion of CO to CO_2* (Bosch process) :

The water gas is mixed with twice its volume of steam and the mixture is passed over a mixture of *ferric oxide* and *chromic oxide* heated at 500°C. Ferric oxide acts as a catalyst and chromic oxide acts as a promoter and accelerates the conversion of CO to CO_2.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 + \text{heat.}$$

In this reversible reaction as the forward reaction is exothermic, the temperature should not exceed 500°C. The forward reaction is carried out by the addition of excess steam and thus most of the CO are converted to CO_2.

(b) The mixture of CO_2 and H_2 thus obtained, is at first pumped into *water under a pressure of 20—30 atmospheres* and then through *caustic soda.* Thus CO_2 present in the mixure is completely removed. The CO present in traces with hydrogen is removed by passing the gas under *200 atmospheric pressure* through a solution of *ammoniacal cuprous formate* and the hydrogen free from CO_2 is collected in gas holders.

3. By the electrolysis of water :

Water is the source of the industrial preparation of hydrogen and oxygen where electricity is cheap.

[A] Principle : Pure water is a bad conductor of electricity and so to make it a good conductor a small amount of dil. H_2SO_4 or 20% solution of NaOH is added to it.

Reactions : NaOH being a strong electrolyte, completely dissociates as Na^+ and OH^- ions in its aqueous solution. Water being a weak electrolyte dissociates to give small amount of H^+ and OH^- ions. When electricity is passed through this solution, hydrogen being less electropositive than sodium, H^+ ions are discharged at the cathode by accepting electrons to produce hydrogen atoms. H atoms combine together to form hydrogen molecules. Thus H_2 gas is liberated at the cathode. The OH^- ions are attracted by the anode where OH^- ions are discharged to produce OH radicals. The OH radicals thus produced react with one another yielding oxygen and water.

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$NaOH \rightleftharpoons Na^+ + OH^-$$

At cathode : $H^+ + e = H$ *At anode :* $OH^- - e = OH$

$H + H = H_2\uparrow$ $4OH = 2H_2O + O_2\uparrow$

As the concentration of H^+ ions are decreased due to their discharge at the cathode, the forward reaction takes place and so more H_2O molecules dissociate to give more H^+ and OH^- ions.

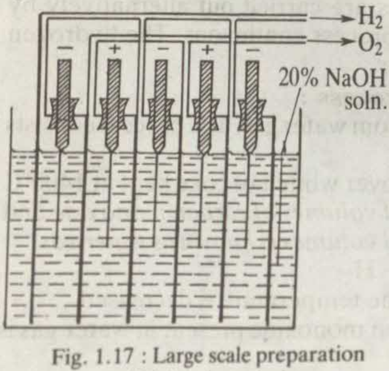


Fig. 1.17 : Large scale preparation of H_2 by electrolysis

[B] Procedure : Electrolysis of water is carried out in a cast iron tank containing 20% NaOH solution. Electric current is passed through this alkaline water by using iron sheets as cathodes and nickel plates as anodes. The cathodes and anodes are kept alternatively in the electrolyte. The electrodes are separated from each other by asbestos partitions. Hydrogen is liberated at the cathode and oxygen at anode. Hydrogen thus obtained is almost pure.

4. From natural gas :

Natural gas contains mostly methane—a hydrocarbon. It is a cheap source of hydrogen. The natural gas is mixed with steam and the mixture is passed over *nickel catalyst* heated to 900°C. Thus methane present in the natural gas is oxidised to give hydrogen and carbon dioxide. The CO_2 is removed by pumping the mixture in water under a pressure of 20—30 atmospheres when CO_2 is completely dissolved in water and hydrogen gas passes out and is collected in gas holders.

$$\underset{\text{Methane}}{CH_4} + 2H_2O = 4H_2 + CO_2$$

5. By the catalytic cracking of higher hydrocarbons :

Hydrogen can also be obtained in a large scale by the catalytic cracking of higher hydrocarbons. As for example *n-heptane* on cracking catalytically yields benzene and hydrogen.

$$\underset{n\text{-heptane}}{C_6H_{14}} \rightarrow \underset{\text{benzene}}{C_6H_6} + 4H_2$$

1.12. Properties of hydrogen.

[A] ?hysical properties :

(i) Hydrogen is a colourless, odourless and tasteless gas.

(ii) *It is the lightest element.* One litre of hydrogen at N.T.P. weighs 0.089 g.

(iii) Hydrogen is almost insoluble in water.

(iv) It can be converted into liquid under high pressure and low temperature, liquid hydrogen boils at $-$ 253°C.

(v) Some metals like *platinum, palladium, cobalt* adsorb a large volume of hydrogen. Palladium can adsorb 936 times of its own volume of hydrogen.

[B] Chemical properties :

1. Combustion : Hydrogen is a combustible gas but not a supporter of combustion. It burns in oxygen or air with a pale blue flame producing water. The mixture of hydrogen and oxygen or air explodes violently on ignition.

$$2H_2 + O_2 = 2H_2O$$

2. Reducing property of hydrogen : Hydrogen has got a great affinity for oxygen and so hydrogen can act as a reducing agent. On being passed over heated metallic oxides, hydrogen removes the oxygen from the oxides and thus reduces them to yield the respective metals. Thus when H_2 is passed over heated *cupric oxide, lead oxide* or *ferric oxide,* it reduces them to produce metallic copper, lead and iron respectively.

$$CuO + H_2 = Cu + H_2O, \qquad PbO + H_2 = Pb + H_2O$$

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$$

3. Action on metals—oxidising property of H_2 : Under suitable conditions hydrogen combines with strong electropositive metals like *sodium, potassium, calcium* etc., yielding their *hydrides.*

Thus, when hydrogen gas is passed over heated sodium, potassium and calcium separately, it combines with them to produce *sodium hydride, potassium hydride* and *calcium hydride* respectively.

These hydrides on being treated with water yield metallic hydroxides liberating hydrogen.

$$2Na + H_2 = 2NaH, \qquad NaH + H_2O = NaOH + H_2\downarrow$$

$$Ca + H_2 = CaH_2, \qquad CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2\downarrow$$

In the formation of these hydrides hydrogen actually accepts electrons from the strong electro-positive metals like Na, K, Ca. As for example, during the formation of NaH, hydrogen accepts one electron from Na atom and the Na atom is oxidised to Na^+ ion and hydrogen is reduced to H^- ion. Thus *in the formation of metallic hydrides hydrogen acts as an oxidising agent.*

$$\begin{array}{llll} Na & -e & = Na^+ & \text{(oxidation)} \\ H & +e & = H^- & \text{(reduction)} \\ Na^+ & +H^- & = NaH & \end{array}$$

$$2\overset{0}{Na} + \overset{0}{H_2} = 2\overset{+1}{Na}\overset{-1}{H}$$

O.N. increased—oxidation

In the above reaction the oxidation number of Na is increased from 0 to +1 and therefore it is oxidised, and this oxidation is brought by H_2. The O. N. of hydrogen is decreased from 0 to −1 ; thus it is reduced.

4. Reaction with non metals : Hydrogen forms stable covalent gaseous hydrides with a number of non metals like halogens, oxygen, nitrogen, sulphur, carbon etc.

(i) **Action on halogens :** Hydrogen reacts with halogens under different conditions.

(a) It combines with *fluorine* even in the dark yielding *hydrogen fluoride.*

(b) Hydrogen combines with *chlorine* in sunlight with the formation of *hydrogen chloride.*

(c) On being heated, *bromine* combines with hydrogen yielding ,*hydrogen bromide.*

(d) It combines with *iodine* in presence of a catalyst with the formation of hydrogen iodide.

$$H_2 + F_2 = 2HF, \qquad H_2 + Cl_2 = 2HCl,$$
$$H_2 + Br_2 = 2HBr, \qquad H_2 + I_2 = 2HI$$

(ii) **Action on nitrogen :** Hydrogen combines with *nitrogen* at 550°C *under 200 atmosphere pressure* in presence of *iron powder as a catalyst* and *molybdenum as a promoter* to produce *ammonia.* the reaction is reversible and exothermic.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat.}$$

(iii) **Action on sulphur :** Hydrogen on being passed through molten sulphur, *hydrogen sulphide* is produced.

$$H_2 + S = H_2S$$

(iv) **Action on carbon :** In presence of *electric spark* hydrogen combines with *carbon* yielding *acetylene.*

$$2C + H_2 = C_2H_2$$

5. Hydrogenation :

In presence of catalysts like *nickel, platinum,* hydrogen combines with many organic compounds. As for examples,

(i) Hydrogen combines with *aldehydes* to yield *alcohols.*

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{Ni cat}]{[2H]} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(ii) Hydrogen combines with *unsaturated hydrocarbons* like *ethelene, acetylene* producing *ethane* which is a *saturated hydrocarbon.*

$$H_2C = CH_2 \xrightarrow[\text{Ni catalyst}]{[2H]} \underset{\text{Ethane}}{H_3C - CH_3}$$

(iii) Hydrogen on being passed through liquid oils which are known as *unsaturated glycerides,* in presence of *finely divided nickel,* combines with them yielding fats which are known as *saturated glycerides.* This process is known as *hydrogenation of oils* used in the manufacture of *vegetable ghee.*

6. Occlusion of hydrogen :

Some metals like *palladium, platinum, gold, iron, nickel,* etc., under certain conditions can dissolve a large volume of hydrogen.

As for example, one volume of palladium can absorb 935 volumes of hydrogen while it is cooled from red hot condition. The absorbed hydrogen by these metals is given off when the metals are heated under reduced pressure.

The phenomenon of absorption of hydrogen by a metal is termed as occlusion and the gas so absorbed by metals, is termed as occluded or adsorbed hydrogen.

Hydrogen possesses the property to dissolve in these metals forming solid solutions. Metals containing occluded hydrogen on being heated pure hydrogen is given off. This property of occluded hydrogen is utilised in the purification of hydrogen gas from other gaseous impurities.

Occluded hydrogen is very active and more powerful reducing agent than the ordinary hydrogen. For examples,

(i) It reacts with chlorine or *iodine* even in the dark.

$$\underset{\text{occluded}}{H_2} + I_2 = 2HI$$

(ii) Ordinary hydrogen cannot reduce yellow solution of ferric chloride, but occluded hydrogen reduces ferric salts to ferrous salts. A piece of palladium which has absorbed hydrogen, when added to a yellow solution of ferric chloride, the solution is readily reduced to give a colourless solution of ferrous chloride.

$$FeCl_3 + \underset{\text{occluded}}{H} = FeCl_2 + HCl$$

(iii) The occluded hydrogen can liberate metallic mercury from mercuric chloride solution. Ordinary H_2 is unable to reduce mercuric chloride solution.

$$HgCl_2 + \underset{\text{occluded}}{2H} = Hg + 2HCl$$

There are different theories which explain the nature of occluded hydrogen.

(i) Holt, Edger (1913) suggested that a part of the occluded hydrogen is present as a condensed layer on the surface of the metals (adsorption) and the rest of the occluded hydrogen dissolves in the interior part of the metal.

(ii) In 1926 Hall suggested that as there was evidence for the existence of two solid solutions which were not miscible, one of this might be a compound e.g., Pd_2H.

(iii) According to the present idea, the occluded hydrogen forms an interstitial compound in which hydrogen probably, in atomic state, occupies the holes in the crystal lattice of the metal and thus forms a solid solution. The high reactivity of occluded hydrogen is due to its atomic state.

- **Difference between adsorption and absorption.**

Adsorption is the process of accumulation of a gas (or any substance) on the surface of another substance. Thus adsorption is a surface phenomenon.

Absorption is a process which involves the diffusion of a gas (or any substance) into the interior of another substance. It is a slow process.

The larger the surface area, the larger will be the adsorption. Thus *palladiam, charcoal, silica gel* are very good adsorbants in finely divided state.

The absorption does not require a large surface area as it is not a surface phenomenon.

1.13. Nascent hydrogen.

A nascent state means a *newly born state.*

- *The nascent state of an element is the state when it is just generated in a chemical reaction from a compound. The hydrogen at the moment of its liberation from a compound is known as nascent hydrogen.*

Nascent hydrogen is far more reactive and powerful reducing agent than the ordinary hydrogen. The reactivity of nascent hydrogen can be shown by the following experiments.

(i) *An acidified solution of potassium permanganate* having *violet colour* is taken in a test tube and ordinary hydrogen from Kipp's apparatus is passed through the solution. Even after a prolonged passing of the gas through the solution, its colour does not change showing that no reaction has taken place. Now to the same solution some pieces of zinc are added when tiny bubbles of hydrogen gas are found to evolve and the violet colour of the solution gradually disappears. This proves that potassium permanganate is reduced by the nascent hydrogen produced by the action of zinc and dil. H_2SO_4 of the solution.

$$\begin{array}{c}
\mathrm{2KMnO_4 = K_2O + 2MnO + 5O} \\
\mathrm{(Zn + H_2SO_4 = ZnSO_4 + 2H) \times 5} \\
\mathrm{10H \quad + \quad 5O \quad = \quad 5H_2O} \\
\mathrm{K_2O \quad + \quad H_2SO_4 \quad = \quad K_2SO_4 \quad + \quad H_2O} \\
\mathrm{2MnO \quad + \quad 2H_2SO_4 \quad = \quad 2MnSO_4 \quad\quad 2H_2O} \\
\hline
\mathrm{2KMnO_4 + 8H_2SO_4 + 5Zn = K_2SO_4 + 2MnSO_4 + 5ZnSO_4 + 8H_2O}
\end{array}$$

(ii) *An acidified solution of potassium dichromate* is taken in a test tube and hydrogen from kipp's apparatus is passed through the solution. Even after passing it through the solution of $K_2Cr_2O_7$, the orange colour of the solution does not change, showing that no reaction has taken place. Now to the same orange solution some pieces of zinc are added. It is observed that the *orange colour of the solution gradually changes to deep green*. Thus, it is proved that $K_2Cr_2O_7$ is reduced to green chromic salt by the nascent hydrogen produced by the action of Zn and acid of the solution.

$$\begin{array}{c}
\mathrm{K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O} \\
\mathrm{(Zn + H_2SO_4 = ZnSO_4 + 2H) \times 3} \\
\mathrm{6H + 3O = 3H_2O} \\
\mathrm{K_2O + H_2SO_4 = K_2SO_4 + H_2O} \\
\mathrm{Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O} \\
\hline
\mathrm{K_2Cr_2O_7 + 3Zn + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3ZnSO_4 + 7H_2O}
\end{array}$$

(iii) Similarly if ordinary hydrogen is passed through the yellow solution of *ferric chloride*, its colour does not change. Now if some pieces of zinc are added to an acidified solution of ferric chloride, it is readily reduced to give a colourless solution of ferrous chloride.

$$\mathrm{FeCl_3 + H = FeCl_2 + HCl}$$

In each of the above reactions, reduction along with the change of colour' is carried out by the nascent hydrogen produced by the action of zinc on dil. H_2SO_4 within the solutions. The ordinary hydrogen i.e., hydrogen in the molecular state, has failed to reduce these coloured solutions.

(iv) Nascent hydrogen produced by the action of zinc and dilute H_2SO_4 can also reduce *potassium chlorate* to *potassium chloride*, and *arsenious chloride* to *arsine*.

$$\begin{array}{c}
\mathrm{KClO_3 + 6H = KCl + 3H_2O} \\
\mathrm{AsCl_3 + 6H = AsH_3 + 3HCl}
\end{array}$$

Some other methods of producing nascent hydrogen :

(a) *By the action of water on sodium amalgam.*

$$\underset{\text{amalgum}}{Na} + H_2O = NaOH + H$$

(b) *By the action of sodium on alcohol.*

$$Na + C_2H_5OH \rightarrow C_2H_5ONa + H$$

(c) *By the action of zinc or aluminium on hot and concentrated solution of NaOH or KOH.*

$$2NaOH + Zn = Na_2ZnO_2 + 2H$$
$$NaOH + Al + H_2O = NaAlO_2 + 3H$$

(d) *By the action of Sn on conc hydrochloric acid.*

$$Sn + 2HCl = SnCl_2 + 2H.$$

Explanations of the enhanced activity of nascent hydrogen :

(i) *Atomic hydrogen theory :* It has been suggested that nascent hydrogen at the moment of its generation exists as single atom or free atom. Free atoms take part in the reaction before they combine together to form molecules. Atoms are more reactive than the molecules and hence nascent hydrogen exhibits its reactivity in different reactions. On the otherhand some work is to be done on the molecules of ordinary hydrogen to split them into single atoms before they can react and as a result they are less reactive. This atomic theory of nascent hydrogen fails to give any explanation for the different degrees of reactivity of nascent hydrogen obtained from different sources. Potassium chlorate, for example, is readily reduced by nacent hydrogen obtained by the action of zinc on dilute sulphuric acid but is unaffected by nascent hydrogen obtained by the action of sodium amalgam on water.

(ii) *Energy theory :* According to this theory nascent hydrogen is activated by the energy liberated in the chemical reaction in which it is generated. Since the chemical reactions which generate hydrogen, liberate different amounts of energy, the difference in the degrees of activity of nascent hydrogen obtained from different sources is due to the different amounts of chemical energy associated with it.

(iii) *Internal pressure theory :* According to this theory the nascent hydrogen at the moment of its liberation remains inside very small bubbles under high pressure due to their small size and as a result it becomes very reactive. It has been found experimentally that the reactivity of ordinary hydrogen is appreciably enhanced by applying great pressure on it.

(iv) Recently the activity of *nascent hydrogen* has been explained on the basis of association of energy during the transfer of electrons from higher electro-positive metals to H^+ ions.

$$Na - e \rightarrow Na^+, \qquad Ca - 2e \rightarrow Ca^{++}$$

The H^+ ions in solutions accept these electrons.

$$H^+ + e = H$$

As the liberation of energy is different in the transfer of electrons in different reactions, the reducing power of nascent hydrogen obtained from different sources are different.

- **Atomic hydrogen :**

In 1925 Langmuir showed experimentally that when thin jet of H_2 gas is passed between two tungsten electrodes producing electric spark (2000°C) at low pressure,

H_2 molecules are dissociated into hydrogen atoms. This dissociation of hydrogen molecules into hydrogen atoms is an endothermic reaction.

$$\underset{\substack{\text{molecular}\\ \text{hydrogen}}}{H_2} \xrightarrow{2000^\circ C} \underset{\substack{\text{atomic}\\ \text{hydrogen}}}{H \quad + H} - 130.7 \text{ k cal.}$$

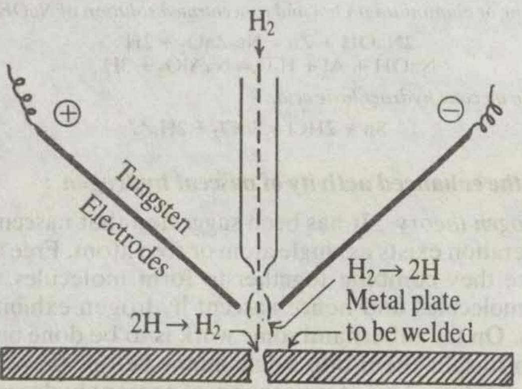


Fig 1.18 : Atomic hydrogen torch

Preparation of atomic hydrogen : Atomic hydrogen can be prepared by *high temperature dissociation method*. In this method thin stream of hydrogen is passed across an arc (2000°C) struck between two electrodes made of tungsten. The greater is the temperature, the greater is the degree of dissociation of molecular hydrogen into atomic hydrogen. The molecular hydrogen dissociates to give off atomic hydrogen by absorbing a large amount of energy.

Properties of atomic hydrogen :

(i) **Stability :** The life period of atomic hydrogen is only one-third of a second. In certain conditions life period of atomic hydrogen can be extended upto 10 seconds.

(ii) Atomic hydrogen combines to give molecular hydrogen, The atomic hydrogen is very unstable, so the atomic hydrogen quickly recombines to produce molecular hydrogen. Platinum, palladium etc., accelerate this unison.

$$H + H \rightleftharpoons H_2 + 103.7 \text{ k cal}$$

Just beyond the electric arc atomic hydrogen combines together to form H_2 molecules and as the forward reaction is an exothermic one, evolves much heat which the atoms had absorbed during the time of dissociation. This heat along with the burning of hydrogen produces a temperature of 5000°C.

(iii) The atomic hydrogen is very active and *at ordinary temperature* it combines with metals like Na K, Li and non metals like S, P, As etc., producing their *hydrides*.

$$Na + H = NaH \; ; \qquad S + 2H = H_2S \; ; \qquad P + 3H = PH_3$$

(iv) **Reducing action :** (a) The atomic hydrogen is very strong reducing agent. It reduces *oxides, chlorides* and *sulphides* of *copper, silver, mercury* etc., to produce the corresponding metals.

$$Ag_2O + 2H = 2Ag + H_2O \; ; \qquad HgO + 2H = Hg + H_2O$$

(b) It can reduce acidified solution $K_2Cr_2O_7$ to chromic salt changing the colour of the solution from orange to green.

It can also reduce the acidified solution of $KMnO_4$ to form colourless solution of manganous salts.

(v) It combines with *oxygen* to produce *hydrogen peroxide.*

$$O_2 + 2H = H_2O_2$$

Uses of atomic hydrogen : The exothermic reaction of the combination of atomic hydrogen to give molecular hydrogen, produces a temperature of 5000°C and so it is used as *atomic hydrogen welding torch,* which is employed for welding metals.

1.14. Allotropy of hydrogen—Ortho and Para hydrogen.

Dennison in 1927 suggested that ordinary hydrogen is a mixture of two forms of hydrogen—*ortho* and *para*. Later on in 1929 Harteck and Bonhveffer experimentally showed that the proportion of the two forms in ordinary hydrogen varies with the change of temperature.

- **Differences between the ortho and para hydrogen :**

(i) *Direction of the spin of the nuclei :* Hydrogen atom consists of a proton which forms its nucleus. Both the proton and the electron have the property of spinning about its axis. A hydrogen molecule consists of two atoms and thus it has got two protons. The two protons in a hydrogen molecule may have their spin either in the same direction or in opposite direction.

The hydrogen molecule, in which the two protons or nuclei spin in the same direction is called ortho hydrogen molecule.

The hydrogen molecule in which the two protons or nuclei spin in the opposite direction, is called para hydrogen molecule.

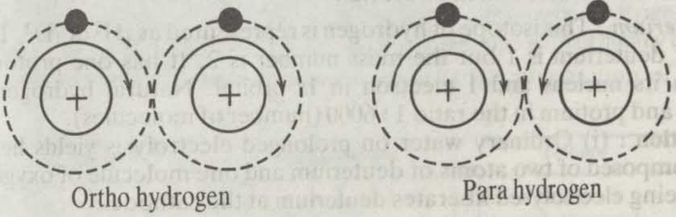


Fig 1.19 :

(ii) *The ortho form is more stable than the para form.* The para form of hydrogen molecule has the tendency to change into the ortho form.

(iii) The two forms are chemically similar but they differ in some physical properties, such as, melting and boiling points, specific heat, thermal conductivity, etc.

(iv) Since the nuclear spins of the para form neutralise each other, the magnetic moment of the para form is zero. The magnetic moment of the ortho form is twice that of proton.

(v) The proportion of ortho and para form in ordinary hydrogen varies with the temperature. At room temperature about 75% ortho hydrogen and 25% para hydrogen are present in ordinary hydrogen. The two forms remain as an equilibrium mixture. At low temperature the portion of para hydrogen increases.

Separation of the two forms :

The ordinary hydrogen at room temperature consists of 75% ortho and 25% para hydrogen. The ordinary hydrogen when passed over activated charcoal kept at 20K, the activated charcoal absorbs only the para form. After this, the absorbed gas is pumped off from the activated charcoal when 99.8% of para hydrogen is given off.

Conversion of para hydrogen to ortho form :

The para form can be converted to ortho form, (i) by heating the para form to 800°C, (ii) by producing electric spark in it, (iii) by passing the para form over platinum or iron catalyst, (iv) by mixing the para form with oxygen or nitrogen dioxide, (v) by adding atomic hydrogen to it. The atomic hydrogen collides with the para hydrogen molecule when the opposite spin of the para form is converted to parallel spin with the formation of the ortho form.

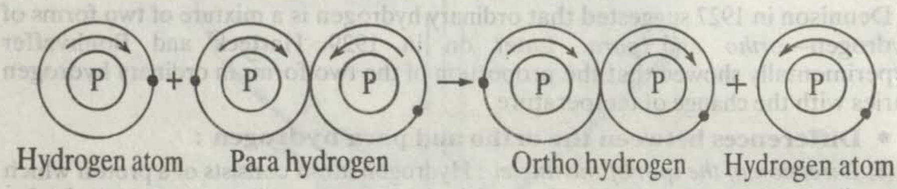


Fig 1.20 :

1.15. Isotopes of hydrogen.

It has been found in the mass spectrograph that hydrogen found in nature consists of the following three isotopes—(i) Ordinary hydrogen or protium H^1, (ii) Deuterium H^2 or D and (iii) Tritium H^3 or T.

(i) *Ordinary hydrogen or protium :* This isotope of hydrogen is represented as ${}_1H^1$. The atomic number of this type is 1 and mass number is 1. It has got one proton at its nucleus and an electron in 1*s* orbital.

(ii) *Deuterium :* This isotope of hydrogen is represented as ${}_1H^2$ or ${}_1D^2$. The atomic number of deuterium is 1 but the mass number is 2. It has one proton and one neutron in its nucleus and 1 electron in 1*s* orbital. Natural hydrogen contains deuterium and protium in the ratio 1 : 6000 (number of molecules).

Preparation : (i) Ordinary water on prolonged electrolysis yields heavy water which is composed of two atoms of deuterium and one molecule of oxygen. Heavy water on being electrolysed liberates deuterium at the cathode.

$$D_2O \rightleftharpoons D^+ + OD^-$$
$$\text{Cathode} : 2D^+ + 2e = D_2$$

(ii) Deuterium may be separated from ordinary hydrogen by means of diffusion. The density of deuterium is twice that of protium. Consequently protium is diffused more faster than deuterium when a mixture of the two are enclosed in clay pipes.

(iii) Deuterium may also be prepared by the action of metallic sodium on heavy water D_2O.

$$2D_2O + 2Na = \underset{\substack{\text{sodium}\\ \text{deutroxide}}}{2NaOD} + D_2$$

Properties : At ordinary temperature deuterium is a colourless, odourless and tasteless gas. It is diatomic. Its melting and boiling points are 18.5 K and 23.4 K, respectively. Its molecular weight is 4.028.

Like ordinary hydrogen deuterium also reacts with oxygen, halogens, nitrogen and the alkali metals to form compounds like D_2O, DCl etc.

$$\begin{aligned}
2D_2 &+ O_2 &&= 2D_2O &&\text{(heavy water)}\\
D_2 &+ Cl_2 &&= 2DCl &&\text{(Deuterium chloride)}\\
3D_2 &+ N_2 &&= 2ND_3 &&\text{(Heavy ammonia)}\\
D_2 &+ 2Na &&= 2NaD &&\text{(Sodium deuteride)}
\end{aligned}$$

Deuterium like ordinary hydrogen forms additive compounds with unsaturated organic compounds.

$$\underset{\text{ethelene}}{H_2C = CH_2} + D_2 \rightarrow \underset{\text{Deutroethane}}{DH_2C - CH_2D}$$

Ordinary hydrogen atoms are replaced by deuterium from compounds containing hydrogen.

$$H_2O + D_2 = D_2O + H_2$$
$$2NH_3 + 3D_2 = 2ND_3 + 3H_2$$
$$CH_4 + 2D_2 = CD_4 + 2H_2$$

Uses : It is used in the preparation of hydrogen bomb and initiating nuclear transformations. Deuterium oxide (heavy water) is used as a moderator in nuclear reactors. It is used in the preparation of deuterium compounds.

(iii) *Tritium :* This type is represented as $_1H^3$ or $_1T^3$. Atomic number of tritium is 1 but its mass number is 3. It has got a proton and 2 neutrons in its nucleus and a single electron is 1*s* orbital.

It is prepared by bombarding deuterium or deuterium compounds or beryllium with accelerated deuterons

$$_1D^2 + {_1D^2} \rightarrow {_1T^3} + {_1H^1}$$
$$_4Be^9 + {_1D^2} \rightarrow {_1T^3} + {_4Be^8}$$

Tritium is a colourless gas. It is radioactive and a β ray emitter. The half life period of tritium is 12.4 years. The melting and boiling points of tritium are 20.6 K and 23.6 K. The reactions of tritium are similar to ordinary hydrogen but the reactions are much slower than the corresponding reactions with ordinary hydrogen.

Uses : It is used as a tracer element. It is used in the preparation of hydrogen bomb.

Protium	Deuterium	Tritium
No. of protons = 1 No. of electrons = 1 No. of neutrons = nil Atomic No. = 1 Mass No. = 1	No. of protons = 1 No. of electrons = 1 No. of neutrons = 1 Atomic No. = 1 Mass No. = 2	No. of proton = 1 No. of electrons = 1 No. of neutrons = 2 Atomic No. = 1 Mass No. = 3

- **Some experiments to illustrate some important properties of hydrogen :**

(1) Prove that hydrogen is a reducing agent :

A small quantity of dry cupric oxide is taken in a small porcelain boat and kept inside a combustion tube. Two tubes—one inlet and the other outlet, are fitted with two open ends of the combustion tube through corks. The end of the outlet tube is joined to the side tube of a U-tube. The black cupric oxide inside the combustion tube is strongly heated and a stream of dry hydrogen gas is passed through it. After sometime the black cupric oxide in the porcelain boat is found to be converted into a red residue and a colourless liquid is found to be collected in the U-tube. The burner is removed and the combustion tube is cooled.

The red residue in the boat is taken out and dissolved in dil. HNO_3 when a blue solution is obtained. To the blue solution excess of NH_4OH is added when a deep blue solution of cupro ammonium salt is obtained. This proves that the red residue is metallic copper. Anhydrous white copper sulphate when comes in contract with the colourless liquid of U-tube turns blue. Thus it is proved that the colourless liquid is water and that heated cupric oxide is reduced to metallic copper by hydrogen.

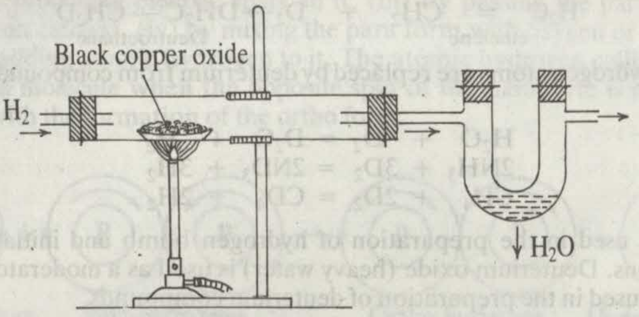


Fig 1.21

$$\underset{\text{black}}{CuO} + H_2 = \underset{\text{red}}{Cu} + H_2O$$

(2) **Prove that hydrogen is lighter than air :**

A gas jar containing air is held over a gas jar full of hydrogen, the two gas jars being separated from each other by a gas jar lid. Now the lid is removed. After some time a lighted taper is introduced into the upper gas jar. It is found that the taper is extinguished but the gas inside the gas jar burns with a blue flame at the mouth of the jar. Now another lighted taper is introduced into lower gas jar. It is found that the taper burns, but the gas inside the gas jar does not burn. This proves that hydrogen gas being lighter than air has displaced the air from the upper one and has occupied the upper gas jar.

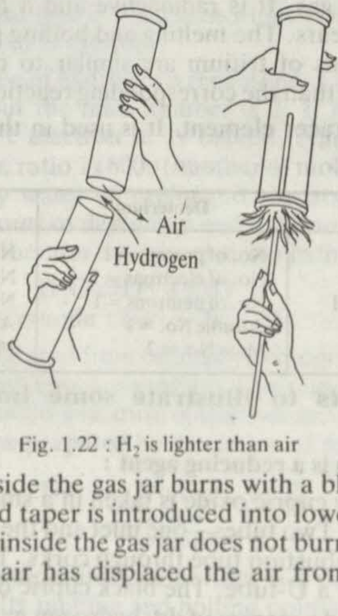


Fig. 1.22 : H_2 is lighter than air

(3) **Prove that hydrogen burns in air or oxygen to form water :**

Hydrogen produced in a Kipps' apparatus is completely dried by passing it through a U-tube containing fused $CaCl_2$. This dry hydrogen is then passed through a jet and ignited. The hydrogen burns with a blue flame. This flame is allowed to touch the cold outer surface of a retort which is kept cold by passing a flow of cold water inside it. After sometime it is found that drops of colourless liquid are formed on the surface of the retort which trickle down in a beaker placed below the retort.

This colourless liquid when brought in contact with anhydrous white copper sulphate, turns blue, showing that the colourless liquid is nothing but water. Thus, it is proved that hydrogen burns in air or oxygen with a blue flame and combines with oxygen forming water.

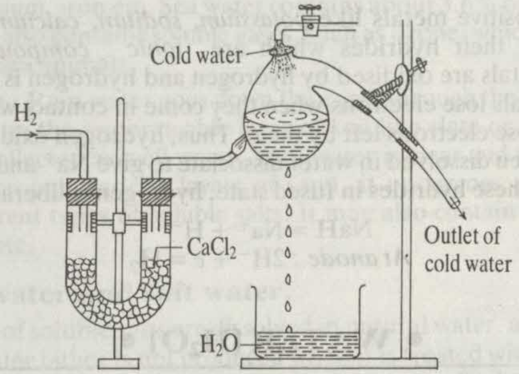


Fig 1.23

(4) **Prove that hydrogen reacts with chlorine to form hydrogen chloride :**

A burning jet of hydrogen is introduced into a gas jar full of dry chlorine. Hydrogen burns in Cl_2 producing white fumes of hydrogen chloride. After some time a little water is added into the gas jar and shaken well. The solution thus produced is taken in a test tube and silver nitrate solution is added to it. A curdy white precipitate is formed which is insoluble in HNO_3, but dissolves in excess of ammonium hydroxide. Thus it is proved that the solution produced in the gas jar is hydrochloric acid, which is produced by the action of hydrogen and chlorine in the gas jar.

- **Uses of hydrogen :**

(1) Hydrogen has a great importance in chemical industries.

(i) *Ammonia* is industrially prepared by the synthesis of N_2 and H_2. (ii) *Hydrochloric acid* is manufactured by the action of hydrogen on chlorine. (iii) *Methanol* is also manufactured by the action of hydrogen on carbon monoxide. (iv) *Unsaturated glycerides* (oils) which are liquid at the ordinary temperature are converted into *saturated glycerides* (fats) by passing hydrogen gas in presence of finely divided nickel at 5 atomspheric pressure and at 150°C—200°C. Hydrogenated oil thus produced is called *vegetable ghee*. Inedible oils are similarly converted to fats which are used in the manufacture of soaps. (v) Hydrogen is also used as petrol substituent by its action on powdered coal.

(2) As the heat of combustion of hydrogen is high enough, it is used as *fuel*. Hydrogen when burnt in oxygen, *oxy-hydrogen flame* is obtained which produces a temperature of 2800°C and so it is used for welding purpose and for melting platinum and quartz. It is also used as *hydrogen torch* for producing a temperature of 5000°C.

(3) Hydrogen is also used as *fuel in rockets and missiles*.

(4) It is used in filling *air ships and balloons*.

(5) It is also used in metallurgy *for the extraction of metals* from their oxides.

(6) It is used as *reducing agent*.

- **Tests for hydrogen :**

(i) Hydrogen burns in air or oxygen with a blue flame producing water which does not change the colour of litmus but turns white anhydrous $CuSO_4$ blue.

(ii) H_2 is adsorbed by palladium, platinum, nickel etc.

- **Oxidising action of hydrogen :**

Strong eletro-positive metals like *potassium, sodium, calcium* etc., react with hydrogen forming their hydrides which are *ionic compounds.* During the reactions these metals are oxidised by hydrogen and hydrogen is reduced by these metals. These metals lose electrons when they come in contact with hydrogen and hydrogen gains those electrons left by them. Thus, hydrogen oxidises these metals. These hydrides when dissolved in water dissociate to give Na^+ and H^- ions. During the electrolysis of these hydrides in fused state, hydrogen is liberated at the anode.

$$NaH = Na^+ + H^-$$

$$\textit{At anode}: 2H^- + e = H_2$$

• WATER [H_2O] •

Mol. wt. = 18	Vap. density = 9	Sp. gr = 1

Water is most abundantly found in nature. As solid it occurs on the mountain peaks and in Artic region. As liquid it is present in oceans, rivers, lakes and ponds. It also occurs below the surface as subsoil water. It is also abundantly found in gaseous state in the atmosphere. Minerals and crystalline compounds contain water as water of crystallisation.

Previously it was regarded as an element. In 1781 Cavendish first proved that it was actually a chemical compound. He prepared it by the action of hydrogen and oxygen in presence of electric spark.

1.16. Natural sources of water.

According to the source, natural water may be classified as follows.

(1) **Rain water :** It is the purest form of natural water. It is obtained by the natural processes of distillation, evaporation and condensation. When it comes down through the atmosphere, it dissolves various kinds of impurities like oxygen, NO_2, CO_2, traces of HNO_3, HNO_2 and NH_3, dust and particles of organic matters. The first shower of rain consists most of these impurities. Rain water is soft water.

(2) **River water :** Snow on the mountain is melted by the sun and the molten ice in the form of stream flows on the surface of earth. These streams are also fed by rain water. So river water contains additional impurities dissolved from the soil and rock. Thus the river water contains both soluble and suspended impurities of organic and inorganic nature. The rain water contains *chlorides, sulphates, carbonates, bicarbonates of Na, K, Ca, Mg and Fe.* In addition to these, the river water contains the impurities from the sewages and sludges of the places through which it flows. It is also contaminated with bacteria of various types. It is generally turbid due to the presence of suspended clay particles.

(3) **Spring water :** A part of rain water goes into the earth through soil, gravel and chalk, etc. It reaches the impermeable layer of soil (clay, slate etc.) and is deposited on that layer. The water thus collected comes out on the surface through any hole as a spring. It is contaminated with some soluble gases and dissolved salts while passing through the ground. This makes the spring water pleasant for drinking. In some springs the minerals and soluble gases like CO_2, SO_2, H_2S etc., remain dissolved in water in sufficient quantity which makes the water to have peculiar smell and taste.

This water is then called *mineral water*. Mineral water is used as medicine. Spring waters which contain sulphate or chloride of magnesium are called saline water.

(4) **Sea water :** All impurities carried by natural water finally go into the sea. Consequently the sea water contains maximum amount of dissolved salts like sulphates, chlorides, bicarbonates, bromides, and iodides of sodium, potassium, calcium, magnesium, iron etc. Sea water contains about 3.6% of these salts of which 2.6% is NaCl. It also contains soluble gases, such as ozone, which are very useful for the existence of sea animals.

(5) **Well water :** Rain water goes down the earth through the porous strata of soil and is collected on the impermeable layer of soil like slate or clay etc. This water under earth is collected as well water. Well water is clear and transparent because while passing through various layers of sand, it undergoes natural filtration. It consists of different types of soluble salts. It may also contain dissolved gases like CO_2, H_2S, SO_2 etc.

1.17. Hard water and soft water.

Various types of soluble salts are dissolved in natural water, as a result of which in some natural water lather is not produced when it is treated with soap.

Water is classified as *hard water* and *soft water* depending on its behaviour with soap.

Soft water : *Water which dissolves soap and readily produces lather is called soft water.*

Hard water : *Water which reacts with the soap solution forming a white scum only instead of producing lather is said to be hard water. Hard water produces lather after consuming a considerable amount of soap.*

- **Causes of hardness of water :**

The hardness of water is due to the presence of dissolved salts like the *chlorides*, *sulphates* and *bicarbonates* of *calcium*, *magnesium* and *iron* which reacts with soap to form curdy white precipitate of insoluble salts.

The soaps are ordinarily the soluble salts of higher fatty acids like *palmitic* ($C_{15}H_{31}COOH$), *stearic* ($C_{17}H_{35}COOH$) and *oleic* ($C_{17}H_{33}COOH$) e.g., sodium palmitate, sodium stearate and sodium oleate. Thus, sodium stearate is a soap which is soluble in water. Sodium stearate (soap) on being treated with the calcium, magnesium and iron salts present in hard water, forms insoluble stearates of calcium, magnesium and iron which separate out from water as curdy white precipitate. Soap is thus consumed in forming the insoluble precipitates of Ca, Mg and Fe salts. The reactions of hard water with soap are given below :—

$$\underset{\substack{\text{present in}\\\text{hard water}}}{CaCl_2} + \underset{\substack{\text{sod. stearate}\\\text{(soap)}}}{2C_{17}H_{35}COONa} \rightarrow 2NaCl + \underset{\substack{\text{Calcium stearate}\\\text{white ppt.}}}{Ca(C_{17}H_{35}COO)_2\downarrow}$$

$$\underset{\substack{\text{present in}\\\text{hard water}}}{MgSO_4} + \underset{\text{Sod. palmitate (soap)}}{2C_{15}H_{31}COONa} \rightarrow Na_2SO_4 + \underset{\substack{\text{Magnesium palmitate}\\\text{white ppt.}}}{Mg(C_{15}H_{31}COO)_2\downarrow}$$

As a result, soap does not produce any lather as long as this precipitation goes on. When all the Ca^{++}, Mg^{++} and Fe^{++} ions are removed from hard water, then only soap produces lather. Thus after a considerable amount of wastage of soap, lathers are produced when soap is treated with hard water.

Thus on the basis of chemical behaviour of hard and soft water their definitions may be expressed as follows :—

Soft water : *Water which contains dissolved salts of metals, like Na or K and which contains very little or no soluble salts of calcium, magnesium or iron in it, is said to be soft water.*

Hard water : *Water which contains dissolved salts like, bicarbonates, chlorides and sulphates of calcium, magnesium and iron, is said to be hard water.*

[**N.B.** A sample of water containing HCl or H_2SO_4 reacts with soap solution (Na-stearate, or Na-palmitate or Na-oleate) to produce their corresponding free acids. As these acids (stearic, palmitic or oleic acid) are insoluble in water, separate from water as precipitates. This leads to the wastage of soap and delayed lathering. Hence such sample of water is hard water.

The aqueous solution of $ZnSO_4$ or $Al_2(SO_4)_3$ is also hard water as it would lead to the formation of insoluble Zn-stearate or Al-stearate which seperates out as an insoluble residue leading to the delayed formation of lather]

- **Types of hardness of water :**

Hardness of water is of two types : (i) **Temporary hardness,** (ii) **Permanent hardness.**

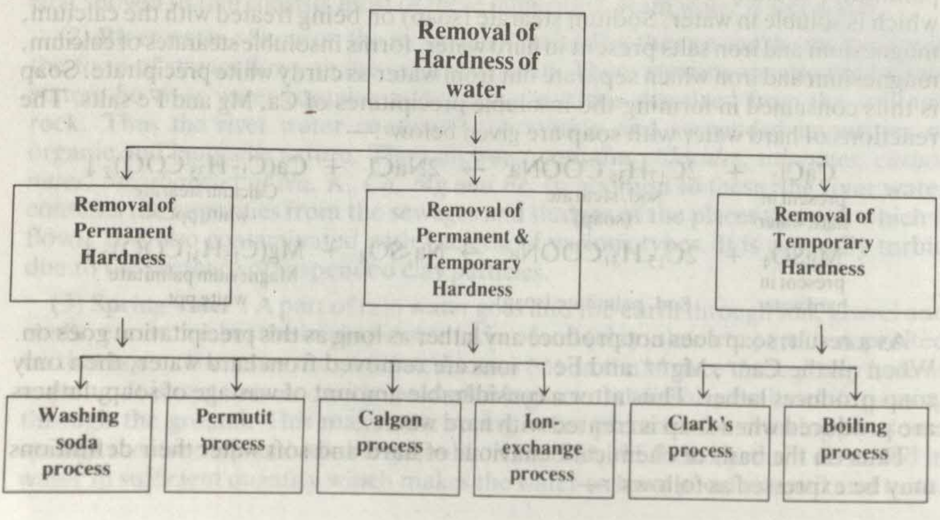
(i) **Temporary hardness :** *Hardness of water due to the presence of soluble bicarbonates of calcium, magnesium and iron, is called temporary hardness and the water of such type is called temporary hard water.* Temporary hardness of water can be removed by simple process like boiling.

(ii) **Permanent hardness :** *Hardness of water due to the presence of soluble chlorides, sulphates of calcium, magnesium and iron is called permanent hardness and the water of this type is called permanent hard water.* This type of hardness of water can not be removed by simple process like boiling.

1·18. Removal of Hardness of water.

The removal of hardness of water is called the *softening of water* or *water softening.*

The hardness of water is due to the presence of dissolved bicarbonates, chlorides and sulphates of Ca, Mg and Fe in water. If by any process or by any chemical reaction the soluble bicarbonates, chlorides and sulphates of Ca, Mg and Fe present in hard water, are converted into insoluble salts and are removed from water as precipites, the water which is left becomes soft.


Removal of Hardness of water
Removal of Permanent Hardness
Removal of Permanent & Temporary Hardness
Removal of Temporary Hardness
Washing soda process
Permutit process
Calgon process
Ion-exchange process
Clark's process
Boiling process

(A) Softening of temporary hard water :

In temporary hard water $Ca(HCO_3)_2$, $Mg(HCO_3)_2$ and $Fe(HCO_3)_2$ are present as soluble bicarbonates. There are two processes of softening temporary hardness of water.

(1) **By boiling :** The soluble bicarbonates present in water, decompose on boiling and are precipitated as insoluble carbonates which are allowed to settle down and filtered off.

$$Ca(HCO_3)_2 = CaCO_3\downarrow + CO_2 + H_2O$$
$$Mg(HCO_3)_2 = MgCO_3\downarrow + CO_2 + H_2O$$
$$Fe(HCO_3)_2 = FeCO_3\downarrow + CO_2 + H_2O$$

Ferrous bicarbonate is very easily oxidised by the oxygen of air to from ferric hydroxide and so the iron is precipitated as ferric hydroxide and thus gets separated from the hard water.

$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3\downarrow + 4CO_2$$

As magnesium carbonate is not completely insoluble in water, hardness due to the presence of $Mg(HCO_3)_2$ cannot be completely removed by simple boiling process.

(2) **Clark's process :** Temporary hardness of water can be removed by *adding requisite quantity of slaked lime* with hard water. Calculated amount of slaked lime should be added, otherwise the excess of the slaked lime will absorb CO_2 of air to form soluble $Ca(HCO_3)_2$ which goes into water making it hard again.

$$Ca(OH)_2 + 2CO_2 = Ca(HCO_3)_2.$$

By the addition of calculated quantity of slaked lime the soluble bicarbonates are converted to form insoluble carbonates which settle at the bottom and are removed.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$

(B) Softening of permanent hard water :

Permanent hardness of water is due to the presence of *chlorides, sulphates, nitrates* of Ca, Mg, Fe etc. Such type to water may be softened by the following processes.

(1) **By the addition of washing soda :**

Permanent hard water may be softened by adding *sodium carbonate* to it, when calcium and magnesium chlorides, sulphates are converted to their insoluble carbonates and are precipitated. The insoluble carbonates are removed by filtration and soft water is obtained as filtrate.

$$CaCl_2 + Na_2CO_3 = CaCO_3\downarrow = 2NaCl$$
$$MgCl_2 + Na_2CO_3 = MgCO_3\downarrow = 2NaCl$$
$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow = Na_2SO_4$$

(2) **Lime Soda process :**

Lime and sodium carbonate are mixed together and the mixture is called lime soda mixture. This lime soda mixture is added to permanent as well as temporary hard water. As a result, both the temporary and permanent hard water are softened by the production of insoluble carbonates which get precipitated and are thus removed from the water. A little NaOH is added to facilitate the precipitation.

$$CaCl_2 + Na_2CO_3 = CaCO_3\downarrow + 2NaCl$$
$$CaSO_4 + Na_2CO_3 = CaCO_3\downarrow + 2Na_2SO_4$$
$$MgCl_2 + Na_2CO_3 = MgCO_3\downarrow + 2NaCl$$
$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O$$

As $MgCO_3$ is slightly soluble in water, hardness due to magnesium salt is removed by the following reactions—

$$MgSO_4 + 2NaOH = Mg(OH)_2\downarrow + Na_2SO_4$$
$$Mg(HCO_3)_2 + 2NaOH = Mg(OH)_2\downarrow + 2NaHCO_3$$

(3) By Permutit process :

This process is extensively used in softening both temporary and permanent hard water on a large scale.

Zeolites are naturally occuring minerals and are complex substances containing sodium and aluminium silicate. The sodium ions in a giant molecule of zeolite, are free to move and so when hard water is allowed to flow over zeolite, the sodium ions are displaced by Ca^{++}, Mg^{++} or Fe^{++} ions of hard water. As zeolites are insoluble in water, the Ca^{++}, Mg^{++} and Fe^{++} ions in hard water are removed and thus hard water is made soft.

Permutit is an artificial zeolite. It is obtained in the form of granules by fusing *sodium carbonate, alumina* and *silica*. Chemically it is *sodium aluminium ortho silicate* ($Na_2Al_2Si_2O_8, x\,H_2O$).

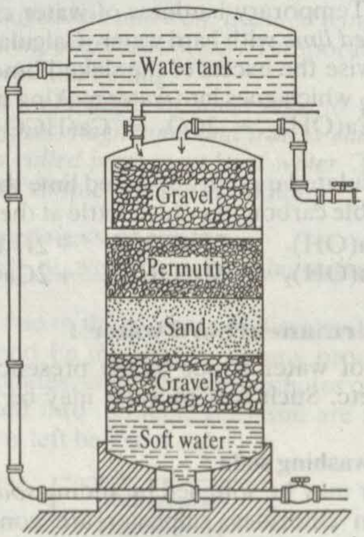


Fig. 1.24 : Permutit process of softening water.

The water softening plant by permutit process consists of a large cylindrical vessel made of iron or bricks. The vessel is packed with layers of *gravel, sodium permutit, fine sand* and *coarse sand* from top to bottom in the order mentioned. Hard water is allowed percolate from the top through the different layers. While passing through the layer of permutit, the calcium, magnesium and iron ions of hard water are exchanged by the Na^+ ions of the permutit i.e., the sodium ions of the permutit react with the soluble calcium, magnesium and iron salts of hard water forming insoluble permutit salts of Ca, Mg and Fe and are retained in the bed. The softened water passes through the different filter beds and comes out of the vessel through an outlet at the bottom. The chemical reactions involved in the process may be represented as follows :—

$$Na_2(\text{Permutit}) + CaCl_2 = \text{Ca Permutit}\downarrow + 2NaCl$$
$$Na_2(\text{Permutit}) + MgSO_4 = \text{Mg Permutit}\downarrow + Na_2SO_4$$

$$Na_2(\text{Permutit}) + MgCl_2 = \text{Mg Permutit}\downarrow + 2NaCl$$
$$Na_2(\text{Permutit}) + Ca(HCO_3)_2 = \text{Ca Permutit}\downarrow + 2NaHCO_3$$

After long use, the sodium permutit loses its ability to soften hard water as most of the Na^+ ions of the permutit are replaced by Ca^{++}, Mg^{++} and Fe^{++} ions of hard water. The inactive permutit is reactivated by passing a strong solution of *sodium chloride* (10%) through the inactive permutit. By this process, the Ca^{++}, Mg^{++}, Fe^{++} ions of the inactive permutit are replaced by Na^+ ions of NaCl solution. Thus, the original sodium permutit is generated again in the bed which is satisfactorily used again.

$$\text{Ca Permutit} + 2NaCl = Na_2\,\text{Permutit} + CaCl_2$$
$$\text{Mg Permutit} + 2NaCl = Na_2\,\text{Permutit} + MgCl_2$$

The permutit process of softening water is also known as *base exchange* or *zeolite process*.

(4) **Ion exchange resin process :**

Various kinds of synthetic organic substances known as ion exchange resins, are now a days widely used for softening hard water. The rasin consists of giant molecules having sulphonic acid group ($-SO_3H$).

At first NaCl solution is allowed to flow through these resin granules when H^+ ions of the $—SO_3H$ group of the resin are replaced by Na^+ ions of NaCl. The sodium compound of the resin thus produced is used as water softener. Hard water containing the soluble salts of Ca, Mg and Fe, is allowed to percolate through a layer of the sodium compound of the resin when Ca^{++}, Mg^{++} and Fe^{++} ions present in hard water, are replaced by Na^+ ions of the resin. The outcoming water is soft water as it becomes free from Ca^{++}, Mg^{++} and Fe^{++} ions.

$$\underset{\text{resin}}{R-SO_3H} + NaCl = R-SO_3Na + HCl \quad [\text{R stands for resin anion}]$$
$$2R-SO_3Na + Ca^{++} = (R-SO_3)_2Ca\downarrow + 2Na^+$$
$$2R-SO_3Na + Mg^{++} = (R-SO_3)_2Mg\downarrow + 2Na^+$$

After long use the rasin loses its activity. The activity is revived again by passing NaCl solution through the inactive rasins.

$$(R-SO_3)_2Ca + 2NaCl = 2R-SO_3Na + CaCl_2$$

(5) **Demineralisation or deionisation of water by ion exchange resins.**

Water, softened by any of the processes described above, is not free from soluble minerals—metallic and non metallic ions remain in the soft water produced by these methods. As for example $CaCl_2$ is present in hard water and this when treated with Na_2CO_3, the soluble $CaCl_2$ reacts with Na_2CO_3 forming insoluble $CaCO_3$ and NaCl. The $CaCO_3$ is removed by filtration but Na^+ and Cl^- ions remain in the soft water thus produced.

Recently ion exchange resins have been employed in removing all the metallic and non metallic ions from water. Hard water is passed in succession through two different types of organic resins. These are called **ion exchange resins.**

(i) *The resins which are used to remove the metallic ions or the cations from water are called cation exchangers.* The cation exchanger contions H^+ ions obtained usually from $-COOH$ or $-SO_3H$ group present in their molecules. These type of resins may be represented by R^-H^+.

(ii) *The resins which are used to remove the non metallic ions or anions from water, are known as anion exchangers.*

The anion exchanger resins are organic *amino ($-NH_2$) compounds* of giant molecules. This type of resins can be represented as $R-NH_2$. The resins are synthetically prepared—they are *insoluble* and *complex organic* substances.

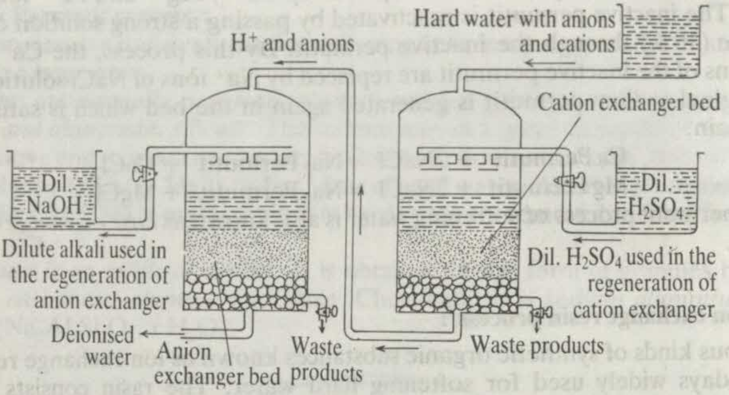

Hard water with anions and cations
H^+ and anions
Cation exchanger bed
Dil. NaOH
Dil. H_2SO_4
Dilute alkali used in the regeneration of anion exchanger
Dil. H_2SO_4 used in the regeneration of cation exchanger
Deionised water
Anion exchanger bed
Waste products
Waste products

Fig 1.25 :

(iii) **Process of de-ionisation :** The process of de-ionisation is carried out by two steps—

(a) *In the first step,* water containing soluble salts, is allowed to flow through a tank partly filled with the granules of cation exchanger. At this, all cations like Ca^{++}, Mg^{++}, Fe^{++} and Na^+ etc., present in water are replaced by the H^+ ions present in the resins and thus removed from water. By this process water becomes acidic. Thus water flowing out of this tank becomes free from any metallic ions.

$$2R^-H^+ + CaCl_2 = R_2Ca \downarrow + 2H^+ + 2Cl^-$$
$$2R^-H^+ + MgSO_4 = R_2Mg \downarrow + 2H^+ + SO_4^{--}$$
$$2R^-H^+ + Ca(HCO_3)_2 = R_2Ca \downarrow + 4H^+ + 2CO_3^{--}$$
$$R^-H^+ + Na^+ = RNa \downarrow + H^+$$

After this treatment, water becomes free from metallic ions but it contains H^+ as the only cation and other anions such as Cl^-, SO_4^{--}, CO_3^{--}, HCO_3^- etc.

(b) *In the second step,* the water coming out of the first tank is passed through a second tank partly filled with the granules of anion exchanger. At first the resin $R-NH_2$ in contact with water is converted to $R-NH_3^+$ group with basic group OH^- attached to it. Here all the anions present in water are exchanged by OH^- ions of the anion exchanger resin.

$$R-NH_2 + H-OH = R\,NH_3^+ + OH^-$$
$$RNH_3^+OH^- + Cl^- = RNH_3Cl \downarrow + OH^-$$
$$2RNH_3^+OH^- + SO_4^{--} = (RNH_3)_2SO_4 \downarrow + 2OH^-$$
$$H^+ + OH^- = H_2O$$

All other non metallic ions present in water are thus eliminated. The OH^- ions thus liberated react with H^+ ions producing water. Thus by this process *a completely demineralised water is obtained which is as good as distilled water.*

Thus, water of the quality of distilled water can be obtained without distillation simply by allowing water to pass through the two types of ion exchangers.

(iv) After prolonged use, both types of resins lose their activity to remove the cations and anions from water. The inactive cation exchangers are reactivated by passing a dilute solution of H_2SO_4 through it and the inactive anion exchanger resins are reactivated by passing dilute NaOH solution through it.

$$R_2Ca + H_2SO_4 = 2R^-H^+ + CaSO_4\downarrow$$
$$RNH_3Cl + NaOH = RNH_3^+ + OH^- + NaCl$$

- **Deionised water and distilled water.**

Practically speaking, distilled water is purer than deionised water. It is because of the fact that, though deionised water is completely freed from all the dissolved electrolytes, yet it contains traces of silica, as the anion exchange resin does not remove silica. It also contains some soluble organic matters (non-electrolytes) and some dissolved gases (CO_2, O_2). But the distilled water is not only freed from all the electrolytes but also freed from silica, and organic matters. It may contain traces of dissolved CO_2. Consequently distilled water is superior to deionised water as far as the purity is concerned. As pyrogen is present in deionised water, it can not be injected like distilled water. The degree of hardness of both deionised and distilled water is O.

[*Calgon,* the trade name of *sodium hexameta phosphate* [$(NaPO_3)_6$] is also used to soften hard water. Ca^{++} and Mg^{++} present in hard water react with Calgon to give complex negative ions which do not form precipitate with soap.

Ethelene diamine tetra acetic acid (E.D.T.A.) removes Ca^{++} and Mg^{++} present in hard water by forming soluble complexes.]

- **Comparison between permutit process and ion exchange resin process :**

(i) Both the processes soften water by ion exchange.

(ii) The permutit process is a base exchange process where the Ca^{++}, Mg^{++}, Fe^{++} ions are exchanged by Na^+ ions of the permutit, while in the deionisation of water by ion exchange resin process Ca^{++}, Mg^{++}, Fe^{++}, Na^+ etc., ions are exchanged by H^+ ions.

(iii) In the permutit process Na^+ ions and the anions are not removed from water, but in ion exchange resin process both the metallic and non metallic ions are completely removed from water.

1.19. Estimation of hardness—degree of hardness of water.

The degree of hardness of a sample of water depends on the amount of soluble salts like calcium, magnesium etc., present in a certain volume of water. The relative hardness of a sample of water is expressed in degree of hardness.

- *The degree of hardness is defined as the number of parts by weight of calcium carbonate (or its equivalent) present in 1,000,000 parts by weight of water.*

Thus, the degree of hardness of a sample of water which contains 60 g of magnesium sulphate per million grams of water can be determined as follows :

1 gram mole of $MgSO_4$ = 24 + 32 + 64 = 120 g of $MgSO_4$
1 gram mole of $CaCO_3$ = 12 + 32 + 48 = 100 g of $CaCO_3$
Now 1 gram mole of $MgSO_4$ ≡ 1 gram mole of $CaCO_3$
i.e. 120 g of $MgSO_4$ ≡ 100 g of $CaCO_3$

$$\therefore 60 \text{ g of } MgSO_4 \equiv \frac{100 \times 60}{120} = 50 \text{ g of } CaCO_3$$

Thus it is found that 60 parts by weight of $MgSO_4$ are equivalent to 50 parts by weight of $CaCO_3$. Therefore the degree of hardness of this sample of water = 50 parts per million = 50 ppm.

As the hardness of water can be taken as the soap precipitating power of water which depends on the amounts of Ca, Mg, Fe salts present in it, the degree of hardness of water is determined experimentally by using a standard soap solution. The total hardness of water is estimated by titrating a measured volume of water against a standard soap solution. This soap solution is previously standardized against water containing a known amount of $CaCl_2$. One volume of this standard soap solution is equivalent to 0.001 g of $CaCO_3$. The end point of the titration is reached when the standard soap solution gives a lather which lasts for 1-2 minutes on shaking.

The different degrees of hardness of different water are given below—

(i) *General soft water* = (0−5) ppm.
(ii) *Medium hard water* = (10−20) ppm.
(iii) *Hard water* = (20−30) ppm.
(iv) *Very hard water* = above 30 ppm.

Synthetic detergents : A typical synthetic detergent is produced from complex hydro-carbon of the type C_nH_{2n} (n = 12 to 20). It is at first reacted with conc. H_2SO_4 and the product thus obtained is reacted with NaOH, the sodium salt thus obtained is the detergent. *It is very soluble is water and as its Ca and Mg salts are also soluble in water, it is not affected by hard water.*

• Numeral problems on hardness of water :

1. *In a sample of water, 0·001 mole of magnesium sulphate is present in 1 litre. Find the hardness of that sample.* *[Joint Ent. 1984]*

Ans : The molecular weight of $CaCO_3 = 40 + 12 + 48 = 100$
Equivalent weight of $CaCO_3 = 100/2 = 50$
The molecular weight of $MgSO_4 = 24 + 32 + 64 = 120$
Equivalent weight of $MgSO_4 = 120/2 = 60$
1 mole of $MgSO_4$ = 120 g of $MgSO_4$
0·001 mole of $MgSO_4 = 120 \times 0{\cdot}001 = 0{\cdot}12$ g of $MgSO_4$
Now 1 gram equivalent of $MgSO_4 \equiv$ 1 gram equivalent of $CaCO_3$
i.e. 60 g of $MgSO_4 \equiv$ 50 g of $CaCO_3$

$$\therefore\ 0{\cdot}12 \text{ g of } MgSO_4 \equiv \frac{50 \times 0{\cdot}12}{60} \text{ g of } CaCO_3 = 0{\cdot}1 \text{ g of } CaCO_3$$

1 litre i.e., 1000 cc water contain 0·1 g of $CaCO_3$
i.e., 1000 parts by weight of water contain 0·1 part by weight of $CaCO_3$

$$\therefore\ 10^6 \text{ parts by weight of water contains } \frac{0{\cdot}1 \times 10^6}{1000} \text{ parts by weight of } CaCO_3 = 100 \text{ parts}$$

by weight of $CaCO_3$.
∴ The degree of hardness of the sample of water = 100 ppm.

2. *One litre of a sample of hard water contains 1·62 g of calcium bicarbonate. What amount of lime is needed to remove the hardness of 10^6 litres of such sample ?* *[I.I.T 1969]*

Ans : The hardness of a sample of water which contains $Ca(HCO_3)_2$ is removed by its action on lime.

$$\underset{162}{Ca(HCO_3)_2} + \underset{56}{CaO} = 2\,CaCO_3 + H_2O$$

1 litre of the sample contains 1·62 g of $Ca(HCO_3)_2$
∴ 10^6 litres of the sample contains $1{\cdot}62 \times 10^6$ g of $Ca(HCO_3)_2$
$= 162 \times 10^4$ g of $Ca(HCO_3)_2$
From the chemical reaction it is found that
162 g of $Ca(HCO_3)_2$ is removed by 56 g of CaO

$$162 \times 10^4 \text{ g of } Ca(HCO_3)_2 \text{ is removed by } \frac{56 \times 162 \times 10^4}{162} \text{ g of CaO} = 56 \times 10^4 \text{ g of CaO}$$

i.e., 56×10^4 g or 560 kg of CaO are needed for softening the given sample.

3. *20 milligram of Ca^{++} ions are present in one litre of a given sample of hard water. How many milli equivalents of Na_2CO_3 would be required to soften 1 litre of the sample ?* *[I.I.T. 1980]*

Ans : 1 litre of the sample contains 20 mg = 0·02 g of Ca^{++} ion.
Equivalent weight of Ca^{++} is 40/2 = 20
∴ 20 g Ca = 1 gram equivalent of Ca

i.e., $0{\cdot}02$ g of Ca^{++} in 1 litre $\equiv \frac{0{\cdot}02}{20}$ gram eq. of $Ca^{++} = 10^{-3}$ gram eq. of Ca^{++} in 1 litre.

Now 1 gram equivalent of Ca reacts with 1 gram eq. of Na_2CO_3
i.e. 1 gram equivalent of Ca^{++}/litre $\equiv$ 1 gram eq. of Na_2CO_3/litre
$\therefore$ 10^{-3} gram equivalent of Ca^{++}/litre $\equiv 10^{-3}$ gram eq. of Na_2CO_3/litre
Now 1000 milli equivalent = 1 gram equivalent
$\therefore$ 1 milli equivalent of Ca^{++}/litre $\equiv$ 1 milli equivalent of Na_2CO_3/litre
i.e., 1 milli equivalent of Na_2CO_3 would be required to soften 1 litre of the sample of hard water.

4. *1 litre of a sample of hard water contains 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$. Find the total hardness in terms of parts of $CaCO_3$ per 10^6 parts of water by weight.* *[I.I.T. 1980]*

Ans. Molecular weight of $CaCl_2 = 40 + 2 \times 35{\cdot}5 = 111$
Molecular weight of $MgCl_2 = 24 + 2 \times 35{\cdot}5 = 95$
Molecular weight of $CaCO_3 = 40 + 12 + 3 \times 16 = 100$
$\therefore$ 111 g of $CaCl_2 \equiv$ 100 g of $CaCO_3$
1 g of $CaCl_2 \equiv$ 100/111 g of $CaCO_3$ = $0{\cdot}9$ g of $CaCO_3$
$\therefore$ 1 mg of $CaCl_2 \equiv 0{\cdot}9$ mg of $CaCO_3$
Again 95 g of $MgCl_2 \equiv$ 100 g of $CaCO_3$
1 g of $MgCl_2 \equiv$ 100/95 g of $CaCO_3$ = $1{\cdot}05$ g of $CaCO_3$.
$\therefore$ 1 mg of $MgCl_2 \equiv 1{\cdot}05$ mg of $CaCO_3$
$\therefore$ 1 litre of the sample of hard water contains $(0{\cdot}9 + 1{\cdot}05)$ mg = $1{\cdot}95$ mg of $CaCO_3$.
Now 1 litre or 1000 ml of hard water = 1000 g i.e., 10^6 mg of water.
$\therefore$ The hard water contains $1{\cdot}95$ parts by weight of $CaCO_3$ per 10^6 parts of water by weight.

5. *1 litre of a sample of hard water on analysis is found to contain $0{\cdot}006$ g of $FeCl_3$, $0{\cdot}008$ g of $CaSO_4$, $0{\cdot}01$ g of NaCl and $0{\cdot}01$ g of $MgSO_4$. Determine the degree of hardness of the given sample. Density of water = $1{\cdot}1$ g/ml.*

Ans : Excepting Na^+ ion, the other ions i.e., Fe^{+++}, Ca^{++}, Mg^{++} ions are responsible for the hardness of the given sample of water. The weight of 1 litre of the given sample = $1000 \times 1{\cdot}1 = 1100$ g.
$\therefore$ The amount of $FeCl_3$, $CaSO_4$ and $MgSO_4$ present in 10^6 g of the sample of water are given as follows—

$$\text{Amount of } FeCl_3 = \frac{0{\cdot}006 \times 10^6}{1100} = 5{\cdot}454 \text{ g}$$

$$\text{Amount of } MgSO_4 = \frac{0{\cdot}01 \times 10^6}{1100} = 9{\cdot}09 \text{ g}$$

$$\text{Amount of } CaSO_4 = \frac{0{\cdot}008 \times 10^6}{1100} = 7{\cdot}273 \text{ g}$$

The equivalent weight of $FeCl_3$ = $162{\cdot}5/3 = 54{\cdot}17$
The equivalent weight of $CaSO_4$ = $136/2 = 68$
The equivalent weight of $MgSO_4$ = $120/2 = 60$
The equivalent weight of $CaCO_3$ = $100/2 = 50$

(i) $54{\cdot}17$ g of $FeCl_3 \equiv 50$ g of $CaCO_3$

$$5{\cdot}454 \text{ g of } FeCl_3 \equiv \frac{50 \times 5{\cdot}454}{54{\cdot}17} \text{ g of } CaCO_3 \equiv 5{\cdot}034 \text{ g of } CaCO_3$$

(ii) 68 g of $CaSO_4 \equiv 50$ g of $CaCO_3$

$$7.273 \text{ g of } CaSO_4 \equiv \frac{50 \times 7{\cdot}273}{68} \text{ g of } CaCO_3 \equiv 5{\cdot}348 \text{ g of } CaCO_3$$

(iii) 60 g of $MgSO_4 \equiv 50$ g of $CaCO_3$

$$9{\cdot}09 \text{ g of } MgSO_4 \equiv \frac{50 \times 9{\cdot}09}{60} \text{ g of } CaCO_3 \equiv 7{\cdot}575 \text{ g of } CaCO_3$$

∴ The equivalent amount of $CaCO_3$ in respect to $FeCl_3$, $CaSO_4$ and $MgSO_4$ present in 10^6 g of the sample given $\equiv (5{\cdot}034 + 5{\cdot}348 + 7{\cdot}575)$ g of $CaCO_3 \equiv 17{\cdot}957$ g of $CaCO_3$

∴ The degree of hardness of the given sample of water is 17·957 degree or 17·957 ppm.

6. *500 ml of a sample of water containing $Ca(HCO_3)_2$ was titrated against (N/60) HCl with methyl orange as indicator. 20 ml of the HCl solution was required to neutralise the given sample. Determine the degree of temporary hardness of the given sample.*

Ans : The reaction is given by the following equation :

$$Ca(HCO_3)_2 + 2HCl = CaCl_2 + 2CO_2 + 2H_2O$$

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

Molecular weight of $CaCO_3 = 100$ ∴ Equivalent weight of $CaCO_3 = 100/2 = 50$.

Eq. wt. of $Ca(HCO_3)_2 = 162/2 = 81$

Now 1 equivalent of HCl $= 81 \equiv 1$ equivalent of $Ca(HCO_3)_2 \equiv 1$ equivalent of $CaCO_3$

∴ 1 equivalent of HCl $\equiv 81$ g of $Ca(HCO_3)_2 \equiv 50$ g of $CaCO_3$

i.e., 1000 ml of (N) HCl $\equiv 50$ g of $CaCO_3$

$$1 \text{ ml of (N) acid} \equiv \frac{50}{1000} \text{ g of } CaCO_3 \equiv 0.05 \text{ g of } CaCO_3$$

$$500 \text{ ml of the sample of water} \equiv 20 \text{ ml of N/60 HCl} \equiv \frac{1}{3} \text{ ml of (N) HCl}$$

$$\frac{1}{3} \text{ ml of (N) HCl} \equiv \frac{1}{3} \times 0{\cdot}05 \text{ g of } CaCO_3 \equiv 0{\cdot}016 \text{ g of } CaCO_3$$

∴ 500 ml of the sample contains 0·016 g of $CaCO_3$

∴ 10^6 ml of the sample contains $\dfrac{0{\cdot}016 \times 10^6}{500} = 32$

∴ The degree of hardness = 32 ppm.

• Disadvantages of using hard water :

(1) **In domestic use :** Water is most essential part of our lives. It is used in cooking, bathing, drinking and washing clothes.

(i) Vegetables and pulses do not cook well in hard water. Very hard water spoils the lustre of the utensils. By using hard water while cooking, an incrustation is formed inside the utensils which causes wastage of fuels.

(ii) Hard water is not at all suitable for washing clothes. The Ca and Mg salts present in hard water react with soap to form Ca and Mg salts of the fatty acids. As these salts are insoluble, they come out of water as precipitate and no lather is formed. Thus a part of soap is wasted in the formation of these insoluble soaps. Yellow stains are formed in clothes due to the presence of iron salts in hard water.

(2) **In boiler use :** Hard water must not be used for generating steam in boilers. This is because hard water on boiling precipitates $CaCO_3$ along with other minerals like silica, iron and aluminium oxide etc. These insoluble substances are collected inside the boiler and inside the steam pipe as hard scale. This layer of scale acts as heat insulator and thus much heat is wasted.

The scales deposited inside the boiler and the metal of the boiler expand unequally on heating. At this, cracks are formed on the scales. Through these cracks water reaches the red hot surface of the boiler and is converted to steam suddenly. The high pressure thus produced may cause the boiler to burst.

$CaCl_2$ and $MgCl_2$ present in hard water on hydrolysis produce HCl which corrodes the wall of the boiler slowly and thus its life is shortened.

$$MgCl_2 + H_2O = HCl + Mg(OH)Cl$$

- **Advantages of hard water :**

Hard water is useful in some respects.

(i) Very soft water is tasteless and insipid and so it is not suitable for drinking purpose. The different minerals and salts present in hard water make it tasty. Hard water is thus used in the preparation of wines and other beverages.

(ii) Soft water has the power to dissolve lead from lead pipes. Soluble lead salts are poisonous. $CaSO_4$ present in hard water forms a layer of insoluble $PbSO_4$ inside the pipe and thus lead poisoning is checked by hard water.

(iii) Small amounts of calcium and magnesium salts are very essential for the growth of our body and these are present in hard water. So hard water should be used for drinking purposes.

Drinking water : Drinking water must have the following properties :—

(i) Drinking water must be free from all harmful bacteria.

(ii) Drinking water should be free from dissolved impurities like nitrites, nitrates and ammonia which are of injurious nature.

(iii) There should be no suspended impurities in drinking water.

(iv) Drinking water should be colourless and odourless.

(v) There should be no poisonous impurities in drinking water like lead.

(vi) Small quantities of sodium, potassium, magnesium and calcium salts and some amount of CO_2 must be present in drinking water as their presence is essentially required to make the water tasty and for the growth of the body.

1.20. Purification of drinking water :

The natural water can be converted to drinking water. The purification of natural water is carried out by the following steps.

(1) **Removal of suspended impurities :**

At first water from river, pond etc., are taken in tanks and *alum* is added to it when the suspended impurities with clay particles, particles of sand, aluminium hydroxide and a few bacteria settle down at the bed of the tank. It is then subjected to filtration. In this process the water from the tank containing suspended impurities is made to pass through layers of sand, charcoal, fine gravels, coarse gravels and stones arranged one below the other in iron tanks. Water percolates down these layers and is transferred to the reservoirs.

(2) **Removal of colloidal impurities :**

There are many colloidal impurities present in natural water. To eliminate these impurities, coagulants like alum, $Al_2(SO_4)_3$ or sodium aluminate etc., are used. These substances when added to water containing colloidal matters, produce coagulation i.e., precipitation of the colloidal matters. This process is carried out in big iron tanks. Coagulated matters are filtered off through sand filters.

(3) **Removal of disease producing bacteria :**

It is possible to remove the colloidal and suspended impurities from water by the above methods, but harmful bacteria cannot be eliminated by the above two processes. So after the filtration, water has got to be disinfected to destroy harmful bacteria.

For this purpose *chlorine, bleaching powder, ozone, potassium permanganate* etc., are added to the filtered water.

(i) Chlorine with water liberates nascent oxygen which is a powerful germicide.

$$Cl_2 + H_2O = 2HCl + O\uparrow$$

(ii) $KMnO_4$ when added to water produces nascent oxygen and this nascent oxygen kills the bacteria.

$$2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3O$$

(iii) A current of ozonised oxygen is passed up a tower through which water percolates. O_3 decomposes to give nascent oxygen and this nascent oxygen oxidises the organic matters and destroys bacteria.

$$O_3 = O_2 + O$$

(iv) Bleaching powder is mixed with water in the ratio 1:25. Bleaching powder produces nascent chlorine with water and nascent chlorine destroys the germs present in water.

(v) The filtered water is then exposed to ultra violet rays produced from a mercury vapour lamp. The bacteria present in water are destroyed by the ultra violet rays.

- **Chemically pure water :**

Water which is free from suspended or non volatile soluble impurities can be obtained by distillation. For the use of chemical works the distilled water is used. It is generally prepared by distilling water from a copper or iron vessel and condensing the steam in condenser made of copper. The middle of the distillate is collected for use. The distilled water thus obtained is not chemically pure as it contains some dissolved gases. To remove the dissolved gases in the distilled water, chlorine is passed through it in boiling condition when the organic nitrogeneous matters are driven off. The excess chlorine is removed by boiling the water. The chemically pure water is then redistilled in presence of potassium permanganate and caustic potash. All these processes are carried out in appparatus made of pyrex glass.

1.21. Properties of water.

(A) Physical Properties :

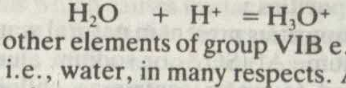
(i) Pure water is colourless, odourless and tasteless liquid at ordinary temperature.
(ii) Pure water freezes at 0°C and boils at 100°C at normal pressure (760 mm of Hg).
(iii) Its density is maximum at 4°C i.e., 1 g/cm^3.
Above and below this temperature its density decreases.

(iv) Water is a weak electrolyte as it ionises very feebly to form H^+ and OH^- ions and so it is a bad conductor of electricity. The H^+ ions formed are taken up by other water molecules to form H_3O^+ ions (hydroxonium ion).

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$H_2O + H^+ = H_3O^+$$

(v) The hydrides of other elements of group VIB e.g., S, Se, Te etc., differ from the hydrides of oxygen i.e., water, in many respects. At ordinary temperature and pressure water is a colourless and odourless liquid while the hydrides of S, Se etc., are gases having bad odour.

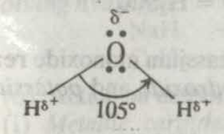
The specific heat, melting point, boiling point, latent heat of water are much greater than those of the hydrides of S, Se, Te etc. As the water molecule is polar, it has a tendency to associate. It exists in the liquid state in combination with other water molecules through hydrogen bond.

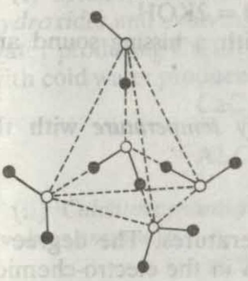


$$\mathrm{H{-}\underset{\underset{H}{|}}{O}\text{----}H{-}\underset{\underset{H}{|}}{O}\text{----}H{-}\underset{\underset{H}{|}}{O}}$$

The association of a number of water molecules with each other increases the effective molecular weight of water and this is manifested in the higher melting and boiling points of water than those of the hydridea of the higher members of group VIB. Many other physical properties of water are abnormal only because of the presence of such hydrogen bonding among its molecules.

(vi) **Structure of water molecule :** Two hydrogen atoms are joined with the oxygen atom by *covalent bond* in water molecule. Because of the strong electro-negativity of oxygen, the electron pairs forming the covalent bonds are attracted by oxygen atom and are brought closer to it. The result of which the oxygen atom in water molecule shares a partial negative charge (δ^-) and each of the hydrogen atoms shares a partial positive charge (δ^+). Due to the presence of two lone pair of electrons in oxygen atom, water molecule becomes 'V' shaped with H — O — H bond angle = 105°.





Thus water molecule becomes polar, with oxygen atom as the negative end and H atoms as the positive end. In the vapour state only single H_2O molecule exists. In the liquid and solid state, the positively charged H atom of one molecule is bonded with negatively charged oxygen atom of the other molecule. Thus water molecules get associated to each other by hydrogen bonds.

The shape of water crystal (ice) is *tetrahedral.* In ice crystal, each H_2O molecule is surrounded tetra-hedrally by 4 other water molecules, being held by hydrogen bonds. There are vacant spaces in the tetrahedral shape of ice crystals. As a result its density becomes less than that of liquid water and so ice floats on water. When the temperature increases from 0°C, the H-bonds start breaking and the H_2O molecules come more closer to each other which becomes maximum at 4°C. So the density of water is maximum at 4°C.

- **Absorption of water :**

Many substances like *conc.* H_2SO_4, *fused* $CaCl_2$, CaO, P_2O_5, *magnesium perchlorate* $[Mg(ClO_4)_2]$, *silica gel* have the capacity to absorb a limited quantity of water. These substances are known as *dehydrating agents* or *dessicants*.

(B) Chemical properties :

(i) Water is *neutral oxide*—it is neutral to litmus.

(ii) It is a *weak electrolyte.* Its conductivity increases by the addition of small amount of acid or alkali.

(iii) In many chemical reactions water *acts as positive catalyst,* e.g. completely dry H_2 and Cl_2 do not react with each other but in presence of moisture they combine readily to form hydrogen chloride.

Phosphorus and sulphur do not burn in perfectly dry O_2 but they burn vigorously in oxygen which contains a little moisture.

(1) **Action on acidic oxides :**

(i) Water soluble acidic oxides like carbon dioxide, sulphur dioxide dissolve in cold water producing *carbonic acid* and *sulphurous acid* respectively. These acids are not stable. The oxides are given off when these acids are heated.

$$CO_2 + H_2O = H_2CO_3 \text{ (carbonic acid)}$$
$$SO_2 + H_2O = H_2SO_3 \text{ (sulphurous acid)}$$

(ii) P_2O_3 combines with cold water producing *phosphorous acid.* P_2O_3 reacts with boiling water producing *phosphine* and *ortho phosphoric acid.*

$$P_2O_3 + 3H_2O = \underset{\text{Phosphorus acid}}{2H_3PO_3}$$
$$2P_2O_3 + \underset{\text{Boiling}}{6H_2O} = \underset{\text{Phosphine}}{PH_3} + \underset{\text{Phosphoric acid}}{3H_3PO_4}$$

(iii) P_2O_5 reacts with *cold water* forming *metaphosphoric acid* and with *boiling water* producing *phosphoric acid.*

$$P_2O_5 + H_2O = \underset{\text{Meta phosphoric acid}}{2HPO_3} \quad ; \quad P_2O_5 + 3H_2O = 2H_3PO_4$$

(iv) N_2O_5 and SO_3 react with water producing *nitric acid* and *sulphuric acid* respectively.

$$N_2O_5 + H_2O = 2HNO_3 \quad ; \quad SO_3 + H_2O = H_2SO_4$$

(2) **Action on basic or metallic oxides :**

(i) The oxides of alkali metals like *sodium monoxide*, potassium monoxide react with water at ordinary temperature producing *sodium hydroxide* and *potassium hydroxide* respectively.

$$Na_2O + H_2O = 2NaOH, \qquad K_2O + H_2O = 2KOH.$$

(ii) *Calcium oxide* (*quick lime*) reacts with water with a hissing sound and generation of heat producing *calcium hydroxide.*

$$CaO + 2H_2O = Ca(OH)_2$$

(iii) *Sodium peroxide* reacts with water at *ordinary temperature* with the evolution of *oxygen* and producing *sodium hydroxide.*

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

(3) **Action on metals :**

Different metals react with water at different temperatures. The degree of reactions of metals with water varies with their position in the electro-chemical series. Metals which are less electro-positive than H_2, do not react with water.

Electro chemical series→

K, Ca, Na	Mg, Al, Zn, Fe	Pb, Cu, Hg, Ag, Au
↓	↓	↓
react with water at ordinary temp.	react with boiling water or steam in red hot	do not react with water

(i) The most electro-positive metals like *sodium, potassium,* react with water vigorously at ordinary temperature forming the corresponding hydroxides and evolving hydrogen. *Calcium* reacts with water comparatively slowly.

$$\begin{aligned} 2Na + 2H_2O &= 2NaOH + H_2 \\ 2K + 2H_2O &= 2KOH + H_2 \\ Ca + 2H_2O &= Ca(OH)_2 + H_2 \end{aligned}$$

(ii) *Powdered metals* like Al and Mg when treated with *boiling water* produce *hydroxides* with the evolution of *hydrogen.*

$$\begin{aligned} 2Al + 6H_2O &= 2Al(OH)_3 + 3H_2 \\ Mg + 2H_2O &= Mg(OH)_2 + H_2 \end{aligned}$$

(iii) When *steam is passed over red hot iron, ferroso ferric* oxide is formed with the evolution of hydrogen. Steam reacts with *hot zinc* forming *zinc oxide* and *hydrogen.*

$$\begin{aligned} 3Fe + 4H_2O &= Fe_3O_4 + 4H_2 \\ Zn + H_2O &= ZnO + H_2 \end{aligned}$$

(4) **Action on non-metals :**

(i) When *steam* is passed over *white hot coke* equal volume of CO and H_2 (*water gas*) are produced.

$$C + H_2O = CO + H_2$$

(ii) *Silicon at white hot condition reacts* with water decomposing it to give *silicon dioxide* and *hydrogen.*

$$Si + 2H_2O = SiO_2 + 2H_2$$

(iii) *Chlorine* combines with water forming *hydrochloric* and *hypochlorous acid.* In sun light the HOCl formed by the above process is decomposed to give off HCl and oxygen.

$$\begin{aligned} Cl_2 + H_2O &= HCl + HOCl \\ 2HOCl &\xrightarrow[\text{Sun light}]{} 2HCl + O_2 \end{aligned}$$

(5) Action on metallic hydrides :

Metallic hydrides react with water producing their corresponding *hydroxides and evolving hydrogen.*

$$\begin{aligned} NaH + H_2O &= NaOH + H_2 \\ CaH_2 + 2H_2O &= Ca(OH)_2 + 2H_2 \end{aligned}$$

(6) Action on metallic carbides :

(i) *Metallic carbides* react with water forming their corresponding *metallic hydroxides* and evolving *different hydrocarbons*. Thus *calcium carbide* reacts with water producing $Ca(OH)_2$ and *Acetylene. Aluminium carbide* when made to react with cold water produces *aluminium hydroxide* and evolves *methane* :

$$\begin{aligned} CaC_2 + 2H_2O &= Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2} \\ Al_4C_3 + 12H_2O &= 4Al(OH)_3 + \underset{\text{Methane}}{3CH_4} \end{aligned}$$

(ii) *Calcium cynamide* when treated with *superheated steam* produces $CaCO_3$ and evolves *ammonia.*

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

(7) Action with metallic nitrides :

Metallic *nitrides* react with boiling water *evolving ammonia* and forming *hydroxides* of those metals.

$$\begin{aligned} Mg_3N_2 + 6H_2O &= 3Mg(OH)_2 + 2NH_3 \\ Ca_3N_2 + 6H_2O &= 3Ca(OH)_2 + 2NH_3 \\ AlN + 3H_2O &= Al(OH)_3 + NH_3 \end{aligned}$$

(8) Action on salts :

Some normal salts when dissolved in water produce either acidic or alkaline solution. This is due to hydrolysis.

$$\begin{aligned} FeCl_3 + 3H_2O &= Fe(OH)_3 + 3HCl\ (\text{Acidic}) \\ Na_2CO_3 + 2H_2O &= 2NaOH + H_2CO_3\ (\text{Alkaline}) \end{aligned}$$

(9) Water is an universal solvent :

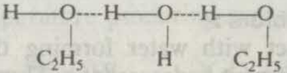
The molecules of water are polar and so it has got the capacity to dissolve both the ionic or polar covalent compounds. Even non-polar covalent compounds like alcohols, carbohydrates etc., dissolve in water. So water is called an *universal solvent.*

(i) **Ionic compounds :** When any ionic compound is treated with water, the negative ends of polar water molecules attract the cations of the ionic compounds and the positive ends of the water molecules attract the anions of the ionic compounds. As for example, Na^+Cl^- is an ionic compound. The positive ends of water molecules attract the Cl^- ions of NaCl and the negative ends attract the Na^+ ions. Thus, both the Cl^- and Na^+ ions are surrounded by water molecules. As a result the attraction between the Na^+ and Cl^- is broken up and they get detached from each other and get into the solution. In addition to this, as the value of the dielectric constant of water is high, the attraction between the opposite ions of the compound becomes weaker when it comes in contact with water and they are easily separated from one another.

(ii) **Polar covalent compounds :** Polar covalent compounds like HCl is soluble in water. When HCl is added to water, the H^+ end of the dipole HCl molecule is detached and is joined to the lone pair of electrons of water molecule forming H_3O^+ (hydroxonium) ion. As a result of which HCl molecule in water dissociates as $(H_3O)^+$ and Cl^- ions and thus gets dissolved in water.

$$HCl + H_2O = H_3O^+ + Cl^-$$

(iii) **Non polar covalent compounds :** Many non polar covalent compounds like alcohols, sugar, glucose etc., though covalent, dissolve in water by the formation of hydrogen bond with the water molecules. Sugar, alcohols etc., have got $-OH$ groups in their molecules and they form hydrogen bond with water molecule by these $-OH$ groups.



(10) **Decomposition of water :**

Ordinarily water is a very stable compound, but it is decomposed to give off its components H_2 and O_2 when it is subjected to electrolysis. It is also decomposed to give H_2 and O_2 when electric spark is passed through steam. It is also decomposed when heated alone at 2500°C to give H_2 and O_2.

- **Detection of water :**

(i) Water can easily be detected by its physical properties. A colourless liquid which freezes at 0°C and boils at 100°C at 760 mm pressure, is water.

(ii) Water when comes in contact with *white anhydrous copper sulphate,* the latter becomes *blue.* By this method traces of water can be detected.

$$\underset{\text{White}}{CuSO_4} + 5H_2O \rightarrow \underset{\text{Blue}}{CuSO_4, 5H_2O}$$

(iii) When water is added to lumps of quick lime, it reacts with water with a hissing sound and with the evolution of heat. The lime swells up and finally crumbles to powder to form slaked lime.

(iv) Water with CaC_2 evolves acetylene gas which burns with a bright luminous flame.

- **Use of water :**

(i) Water is used as solvent. It dissolves almost every substance and for this reason it is called universal solvent.

(ii) Water is indispensible to us for cooking and drinking purpose.

(iii) A larger quantity of water is consumed for washing clothes and other materials.

(iv) Water is used in irrigation.

(v) Water is used in the boilers for running machines and for cooling purpose in the chemical industries.

(vi) It is used in the manufacture of H_2, O_2, acids, alkali and water gas etc.

(vii) It is used as fire extjnguisher.

1·22. Composition of water

The composition of water *by volume* can be determined by (i) *Synthetic method.* (ii) *Analytical method.*

(1) **Volumetric composition of steam.**

(i) Synthetic method [Hofmann's method] :

(A) **Description of apparatus** : (i) The apparatus used in this process consists of a U-shaped eudiometer tube, one end of which is closed and graduated. (ii) At the closed end of the eudiometer tube two platinum wires are sealed into the glass for producing electric spark inside the tube. (iii) The closed limb is sorrounded by a wider tube which serves as a jacket. The jacket is provided with two tubes—one at the top and the other at the bottom. (iv) The other limb of the eudiometer is provided with a stop cock near the bottom. This limb acts as a manometer.

(B) **Procedure :** The closed limb is completely filled with mercury. A mixture of 2 volumes of pure and dry hydrogen and one volume of pure and dry oxygen is introduced into the closed limb by the displacement of mercury. The mixture of hydrogen and oxygen is obtained by the electrolysis of slightly acidified water. The liberating gas is freed from the moisture by passing the gas mixture through concentrated H_2SO_4.

Vapour of Amyl alcohol (b.p. 132°C) is passed through the jacket of the inlet tube at the top of the jacket, which passes out by the lower outlet tube. After sometime the temperature of the gas mixture becomes constant. Now the mercury in the two limbs is brought to the same level. With a view to reducing the pressure inside the closed limb, some mercury is taken out by opening the stop cock. Now the volume of the gas mixture is carefully noted. The open end of the eudiometer is now closed by thumb and the gas mixture is exploded by passing electric spark into it. In presence of the electric spark H_2 and O_2 combine together to form steam. A contraction in the gas mixture takes place after the reaction, so mercury is added to the open tube to bring the mercury to the same level in both the limbs. The volume of steam produced is measured.

(C) **Observation :** It is observed that volume of the steam produced is exactly two-thirds of the volume of the mixture of H_2 and O_2 of the original gas mixture taken.

Now the whole apparatus is allowed to cool to the room temperature. As the apparatus cools, the steam inside the closed limb gets condensed to form water which occupies very negligible volume. So, the mercury level gradually rises up and finally touches the upper end of the limb. Thus it is proved that all the hydrogen and the oxygen which were taken as gas mixture have completely converted to produce steam.

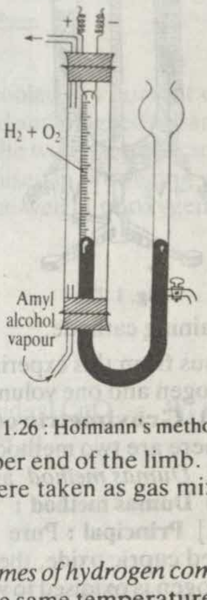


Fig. 1.26 : Hofmann's method

(D) **Conclusion :** In this experiment it is proved that *2 volumes of hydrogen combine with one volume of oxygen to form 2 volumes of steam* at the same temperature and pressure.

(E) **Molecular formula of water :** Two volumes of steam contain 2 volumes of hydrogen and one volume of oxygen. According to Avogadro's hypothesis let *n* be the number of molecules present in one volume.

∴ 2*n* molecules of steam contain 2*n* molecules of hydrogen and *n* molecules of oxygen.

Thus we can write—

2*n* molecules of steam contain 2*n* molecules of hydrogen and *n* molecules of oxygen.

or, 2 molecules of steam contain 2 molecules of hydrogen and 1 molecule of oxygen.

or, 2 molecules of steam contain 4 atoms of hydrogen and 2 atoms of oxygen.

(As hydrogen and oxygen molecules are diatomic).

∴ 1 molecule of steam contains 2 atoms of hydrogen and 1 atom of oxygen.

Therefore, the molecular formula of water or steam is H_2O.

(ii) Analytical Method : Electrolysis of water in a voltameter :

The apparatus used in this process consists of a U-tube. The two limbs of the U-tube are joined with a long necked funnel. The upper end of the two limbs are closed by two stop cocks and both the limbs are graduated. The two limbs are fitted with two platinum electrodes sealed through the glass at the lower portion.

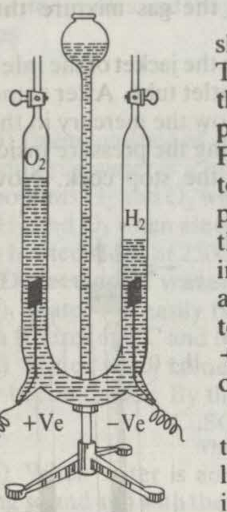


Fig. 1.27 :

By opening the two stop cocks of both the limbs, water slightly acidulated with H_2SO_4 is added through the funnel. The two limbs being completely filled with the electrolyte, the stop cocks are closed. Now on passing electricity current passes from the positive pole of the battery to the anode. From anode it passes through the electrolyte to the cathode, to reach the negative pole of the battery. As the current passes through the electrolyte, H^+ ions are discharged at the cathode with the formation of H_2 and this H_2 is collected in the graduated limb. The OH^- ions are discharged at the anode to form OH radicals. The OH radicals combine together to form O_2 and water at the anode. $4OH = 2H_2O + O_2$. The O_2 thus produced is collected at the other limb of the U-tube.

After some time the passage of current is stopped and the volumes of hydrogen and oxygen collected in the two limbs are measured. It is found that volume of O_2 collected in the graduated limb containing anode is half of the volume of hydrogen gas collected in the other limb containing cathode.

Thus from this experiment it is proved that water is composed of two volumes of hydrogen and one volume of oxygen measured at same temperature and pressure.

[2] Gravimetric composition of water :

There are two methods of finding out the composition of water by weight—

(I) *Dumas method* and (II) *Morley's method.*

(I) Dumas method :

[A] **Principal :** Pure and dry hydrogen when passed over known amount of heated cupric oxide, the cupric oxide is reduced by H_2 to form metallic copper and hydrogen is oxidised to water. From the loss of weight of cupric oxide and the weight of water formed, the weight of hydrogen and oxygen used in the formation of a definite amount of water can be known.

$$CuO + H_2 = Cu + H_2O$$

[B] **Procedure :** Hydrogen prepared in the Kipp's apparatus is purified by passing it through a series of U-tube containing *lead nitrate, silver sulphate solution, sodium hydroxide solution, conc.* H_2SO_4 and finally through a U-tube containing P_2O_5. The pure and dry hydrogen thus prepared is passed through one end of a bulb tube containing dry cupric oxide. The bulb tube with CuO in it is previously weighed. The other end of the bulb tube is joined with a previously weighed U-tube containing fused $CaCl_2$. The free end of this U-tube is joined with a guard tube containing P_2O_5 to prevent the moisture of air to get into the U-tube containing $CaCl_2$. All connections of the apparatus are made air tight. At first the air inside the apparatus is removed by passing pure and dry hydrogen. Now the bulb-tube is strongly heated and the passing of H_2 is continued. While passing over the heated CuO, H_2 combines with O_2 to form steam which passes off and is absorbed in the U-tube containing $CaCl_2$. Black cupric oxide is reduced to form red metallic copper which is left in the bulb tube.

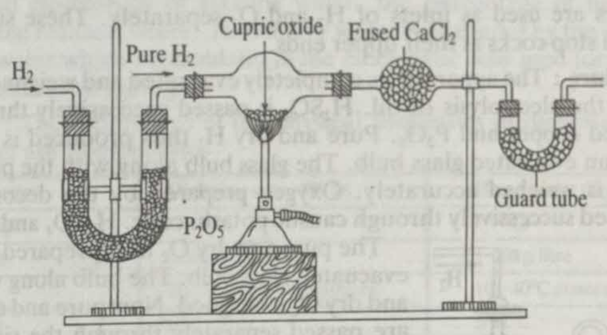


Fig. 1.28 : Duma's method

After the completion of the reaction, the apparatus is cooled in a current of H_2. The bulb tube and the U tube containing $CaCl_2$ are separated and weighed separately. The increase in weight of the U-tube gives the weight of the water formed and the loss of weight in the bulb tube gives the weight of oxygen used in producing water. The weight of hydrogen can be obtained by subtracting the weight of oxygen from the weight of water produced.

[C] **Calculations :**

(i) *Before the experiment—*

The wt. of bulb tube + cupric oxide $= W_1$ g

The wt. of the U-tube containing $CaCl_2$ $= W_2$ g

(ii) *After the experiment—*

The wt. of bulb tube + metallic Cu formed + residual CuO $= W_3$ g

The wt. of U-tube + $CaCl_2$ + water formed $= W_4$ g

$\therefore$ The wt. of water formed $= (W_4 - W_2)$ g

Wt. of used up oxygen $= (W_1 - W_3)$ g

$\therefore$ The wt. of hydrogen which combines with O_2

$= (W_4 - W_2) - (W_1 - W_3) = M$ g (suppose)

It is found that,

M g of hydrogen combines with $(W_1 - W_3)$ g of oxygen to form $(W_4 - W_2)$ g of water.

It is actually found in the experiment that—

$$\frac{\text{Wt. of hydrogen}}{\text{Wt. of oxygen}} = \frac{M}{W_1 - W_3} = \frac{1}{7{\cdot}98}$$

So it may be concluded that 1 part by wt. of hydrogen combines with 8 parts by wt. of oxygen to form 9 parts by wt. of water.

(II) Morley's Method :

[A] **Principle :** This method is based on the synthesis of water from its elements. A known weight of pure hydrogen is made to react with a known weight of pure oxygen to produce water by means of electric spark.

$$2H_2 + O_2 = 2H_2O$$

The gravimetric composition of water is found out from the weights of H_2 and O_2 taken and the weight of water produced by their combination.

[B] **Description of the apparatus :** The apparatus consists of a glass tube which is called *reaction tube*. This tube is connected with two side tubes filled with P_2O_5. The ends of these side tubes are introduced into the reaction tube in the form of jets. Two platinum wires are fused inside the reaction tube near the jets. The upper ends of the side tubes are used as inlets of H_2 and O_2 separately. These side tubes are provided with stop cocks at their upper ends.

[C] **Procedure :** The apparatus is completely evacuated and weighed. The H_2 gas produced by the electrolysis of dil. H_2SO_4 is passed successively through caustic potash, heated copper and P_2O_5. Pure and dry H_2 thus produced is absorbed by palladium in an evacuated glass bulb. The glass bulb along with the palladium and occluded H_2 is weighed accurately. Oxygen prepared by the decomposition of $KClO_3$ is passed successively through caustic potash, conc. H_2SO_4 and P_2O_5. The pure and dry O_2 thus prepared is led into an evacuated glass bulb. The bulb along with the pure and dry O_2 is weighed. Now pure and dry H_2 and O_2 are passed separately through the side tubes and electric spark is produced between the platinum wires. The H_2 combines with the O_2 at the jets to produce steam in the reaction tube which is cooled by immersing it in ice cold water. The steam thus produced gets condensed and collects in the lower part of the reaction-tube. The entries of the two gases into the reaction tube is regulated by the stop cocks so that H_2 and O_2 are introduced into the reaction tube in the ratio 2 : 1 by volume to make their combination effective.

The unreacted gases are pumped out through the side tubes and their corresponding weights are taken. During this process, the loss of water is prevented by the P_2O_5 in the side tubes. The whole apparatus is weighed accurately again. The increase in weight gives the weight of the water produced. The weight of the bulbs containing H_2 and O_2 are weighed again after the completion of the experiment.

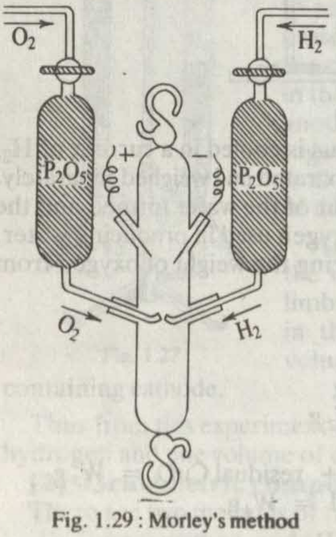


Fig. 1.29 : Morley's method

[D] **Calculations :**

Wt. of the bulb containing the occluded H_2 before experiment = W_1 g

Wt. of the bulb containing H_2 after expt. = W_2 g

∴ Wt. of hydrogen used up into the reaction tube = $(W_1 - W_2)$ g

Wt. of the bulb containing O_2 before expt. = W_3 g

Wt. of the bulb containing O_2 after expt. = W_4 g

∴ The wt. of O_2 used up in the reaction tube = $(W_3 - W_4)$ g

Let the wt. of water produced = W g

From the result of a number of experiments Morely found out that the average of the ratios—

$$\text{H : O} = (W_1 - W_2) : (W_3 - W_4) = 1 : 7{\cdot}9398$$

$$\text{and H : H}_2\text{O} = (W_1 - W_2) : (W) = 1 : 8{\cdot}9395$$

i.e., 8 parts by wt. of O_2 combine with 1 part by wt. of H_2 to produce 9 parts by wt. of H_2O.

1.23. Heavy water or Deuterium oxide.

Heavy water was discovered by Harold C. Urey in 1931.

Heavy hydrogen or deuterium is an isotope of ordinary hydrogen. The atomic mass of deuterium is 2. Heavy water or deuterium oxide is the oxide of deuterium. This is produced by the reaction of deuterium ($_1H^2$) with oxygen. It is present in ordinary water in very small amount (1 part in 6,000 parts by weight approximately). On prolonged electrolysis of alkaline water, the percentage of heavy water is increased in the residual water. Thus heavy water is prepared by the electrolysis of the residual water which accumulates in the electroytic cells used for several years for the preparation of hydrogen.

Properties : The differences in the physical properties of deuterium oxide and ordinary water are given below—

Property	Ordinary water (H_2O)	Heavy water (D_2O)
Molecular weight	18·016	20·028
Density at 20°C	0·988 g/litre	1·106 g/litre
Boiling point	100°C at normal pressure	101·40°C at normal pressure.
Freezing point	0°C	3·82°C
Dielectric const. at 20°C	82	80·5

Heavy water (D_2O) is not radioactive but still it is slightly injurious to some living organism. Taking bath in D_2O causes serious dehydration.

The chemical properties of heavy water are similar to those of ordinary water.

Heavy water is a weaker electrolytic solvent than ordinary water.

(i) Heavy water reacts with *sulphur trioxide* to produce *deutero sulphuric acid.*

$$SO_3 + D_2O = D_2SO_4$$

(ii) Heavy water reacts with *metallic nitrides* to form *metallic oxides* with the evolution of *deutero ammonia.*

$$Mg_3N_2 + 3D_2O = 3MgO + 2ND_3$$

$$2AlN + 3D_2O = Al_2O_3 + 2ND_3$$

(iii) Heavy water reacts with *calcium carbide* to yield *deutero acetylene.*

$$CaC_2 + D_2O \rightarrow C_2D_2 + CaO$$

Uses : (i) It is used for the preparation of heavy hydrogen (D_2) and as a trace compound.

(ii) D_2O is extensively used to control the velocity of neutrons in atomic reactor.

(iii) It is used in the study of mechanism of the chemical reactions in organic chemistry.

• HYDROGEN PEROXIDE (H_2O_2) •

Thenard discovered hydrogen peroxide in 1808. Traces of hydrogen peroxide occurs in air and in water.

1.24. Preparation of hydrogen peroxide.

Laboratory method.

[A] **Principle** : Hydrogen peroxide is prepared in the laboratory by the action of *ice cold dilute sulphuric acid or phosphoric acid* with *ice cold paste of barium peroxide.* Insoluble *barium sulphate* is precipitated with the production of *hydrogen peroxide.*

$$BaO_2 + H_2SO_4 = BaSO_4\downarrow + H_2O_2$$

[B] **Procedure :** (i) A thin paste of *hydrated barium* peroxide (BaO_2, $8H_2O$) is prepared by stirring finely powdered barium peroxide with a small amount of water in a beaker. (ii) Dilute sulphuric acid is prepared by adding *1 volume of conc.* H_2SO_4 *to 5 volumes of water* taken in a beaker. (iii) Both the beakers are cooled to 0°C by placing them in a freezing mixture of ice and common salt. (iv) Now the ice-cold paste of hydrated barium peroxide is slowly added to the ice-cold dilute sulphuric acid and the mixture is continuously stirred with a glass rod. The addition of the BaO_2 paste is continued *till the final solution is slightly acidic,* as the presence of slight acid decreases the rate of decomposition of hydrogen peroxide. By the reaction of barium peroxide with dilute sulphuric acid, insoluble barium sulphate and hydrogen peroxide are produced. (v) The precipitate of barium sulphate settles down and a transparent liquid above the insoluble $BaSO_4$ is collected as filtrate after filtration. The liquid thus obtained is an aqueous solution of hydrogen peroxide containing 10—20% hydrogen peroxide.

[C] **Purification :** Though water is more volatile than hydrogen peroxide (b.p. of $H_2O = 100°C$ and that of $H_2O_2 = 151°C$), it is not possible to separate water from the hydrogen peroxide by fractional distillation as hydrogen peroxide has a tendency to decompose into water and oxygen at a temperature far below its boiling point.

$$2H_2O_2 = 2H_2O + O_2$$

(i) **Removal of water by evaporation.** The aqueous solution of hydrogen peroxide is taken in a smooth porcelain dish and heated to 60°C—70°C on water bath, when water which is more volatile, gradually evaporates out. Thus the concentration of H_2O_2 in the residue becomes 45—60%. Further attempt to concentrate the solution by this process would lead to rapid decomposition of hydrogen peroxide.

(ii) **Distillation under reduced pressure.** The 60% hydrogen peroxide thus obtained is subjected to a repeated fractional distillation at a low pressure of 15 mm at 80°C, when 99% pure hydrogen peroxide is obtained.

(iii) The 99% hydrogen peroxide is then kept in a vacuum desiccator on concentrated sulphuric acid, when the rest of water is removed.

(iv) When the 99% H_2O_2 solution is cooled to −10°C, crystals of pure H_2O_2 separate out from the solution.

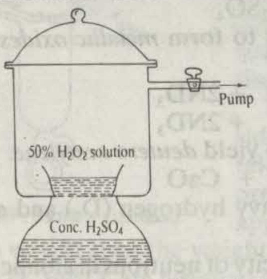


Fig. 1.30 : Concentration of H_2O_2 in vacuum desicator

• **Phosphoric acid is preferred to sulphuric acid in the preparation of H_2O_2 from barium peroxide—explain why.**

This is because of the fact that small amount of barium persulphate is produced by the action of dil. H_2SO_4 with BaO_2 which tends to decompose the produced H_2O_2. On the other hand phosphoric acid precipitates insoluble barium phosphate and at the same time it removes almost all the heavy metals as insoluble phosphates which act as catalysts for the decomposition of H_2O_2. Sulphuric acid can not precipitate these heavy metals from the solution. Moreover H_3PO_4 acts as a good inhibitor (negative catalyst) which retards the decomposition of H_2O_2.

• **Some important points regarding the laboratory method of preparation of H_2O_2.**

(i) *Conc.* H_2SO_4*, conc. HCl or nitric acid are not suitable for the preparation of* H_2O_2 *:*

(a) Hydrogen peroxide is an unstable compound. Due to the presence of *peroxo bond* in its molecule, it tends to decompose into H_2O and O_2 even at room temperature. The decomposition of H_2O_2 is accelerated by heat. When conc. H_2SO_4 is made to react with BaO_2, much heat is evolved and the produced H_2O_2 is decomposed rapidly by the liberated heat. Moreover conc. H_2SO_4 being an oxidising agent gives off nascent oxygen which reacts with the H_2O_2 to give O_2 and water.

$$\begin{array}{c} H_2SO_4 = H_2O + SO_2 + O_2 \\ H_2O_2 + O = H_2O + O_2 \\ \hline H_2SO_4 + H_2O_2 = SO_2 + 2H_2O + O_2 \end{array}$$

Hence ice-cold dilute H_2SO_4 solution is used instead of conc. H_2SO_4 in the preparation of H_2O_2.

(b) Concentrated or dilute HCl reacts with BaO_2 to produce barium chloride and H_2O_2. As $BaCl_2$ is soluble in water, it is not possible to separate $BaCl_2$ from the aqueous solution of H_2O_2. Consequently hydrochloric acid is not suitable for the preparation of H_2O_2.

(c) Nitric acid is an oxidising acid and so it liberates nascent oxygen which reacts with the H_2O_2 produced by the action of nitric acid on BaO_2 to give O_2 and water. Moreover barium nitrate is produced by the action of nitric acid on BaO_2, which is soluble in water. So it is difficult to separate barium nitrate from the aqueous solution of H_2O_2.

$$BaO_2 + 2HNO_3 = Ba(NO_3)_2 + H_2O_2$$
$$2HNO_3 = H_2O + 2NO_2 + O$$
$$H_2O_2 + O = H_2O + O_2$$

(ii) *A thin paste of hydrated barium peroxide is used in the preparation of H_2O_2, instead of anhydrous BaO_2 :*

Anhydrous BaO_2 is not used in the preparation of H_2O_2 because, (a) much heat is evolved by the action of dilute H_2SO_4 on anhydrous BaO_2 which accelerates the decomposition of H_2O_2 as it tends to decompose into H_2O and O_2 due to the presence of peroxo bond in its molecule. (b) As soon as the particles of BaO_2 come in contact with dil. H_2SO_4 a layer of insoluble $BaSO_4$ is produced on the surface of the particles. The insoluble layer thus produced prevents the acid to come in contact with BaO_2 any further and as a result the reaction stops.

A thin paste of finely powdered BaO_2 with water, having the composition BaO_2, $8H_2O$, enables the acid to react with each fine particle and thus there is no chance of ceasation of the reaction by the formation of insoluble layer.

(iii) *The temperature of the acid and BaO_2 paste is kept at 0°C.*

Hydrogen peroxide tends to decompose spontaneously into H_2O and O_2 due to the presence of peroxo bond in its molecule. This decomposition is accelerated by heat. Consequently the temperature of the reactants is lowered down to 0°C resulting in the prevention of the decomposition of H_2O_2.

(iv) *At the end of the reaction between BaO_2 and dil. H_2SO_4 the final solution is kept slightly acidic :*

The decomposition of hydrogen peroxide is retarded by the presence of a trace of an acid which acts as an inhibitor (negative catalyst). If excess of BaO_2 is added, the whole of the acid reacts with BaO_2 and thus used up in producing $BaSO_4$ and H_2O_2. As a result the produced H_2O_2 begins to decompose due to the absence of the negatively catalysing acid. That is why the final solution at the end of the reaction is kept slightly acidic.

(v) *The paste of BaO_2 is added to the acid solution but the reverse is not done :* The paste of barium peroxide is added to the dilute H_2SO_4 with constant stirring. As a result during the reaction between BaO_2 and dil. H_2SO_4, an excess acid is always present in the mixture. Thus the produced H_2O_2 does not decompose due to the presence of traces of acid.

But on the other hand, if the acid is added to the paste of barium peroxide, it reacts with the whole of the acid added. As a result no excess acid would be left there to retard the decomposition of the produced H_2O_2.

1.25. Other methods of preparation of hydrogen peroxide.

(i) By the action of BaO_2 on phosphoric acid :

When barium peroxide is treated with phosphoric acid, hydrogen peroxide and insoluble barium phosphate are produced. At the end of the reaction the final solution is kept slightly acidic. Barium phosphate is separated by filtration when an aqueous solution of hydrogen peroxide is obtained as filtrate.

$$3BaO_2 + 2H_3PO_4 = Ba_3(PO_4)_2 \uparrow + 3H_2O_2$$

(ii) Merck's process :

Hydrogen peroxide is prepared by the action of *carbon dioxide on barium peroxide* suspended in water. This process is known as *Merck's process.*

Finely powdered barium peroxide is taken in a beaker and is suspended in water. The barium peroxide suspension is cooled to 0°C by placing the beaker in a freezing mixture. Carbon dioxide is then passed through the cooled mixture till the solution turns faintly acidic. CO_2 reacts with BaO_2 suspended in water with the formation of H_2O_2 and insoluble barium carbonate. $BaCO_3$ is filtered off when aqueous solution of hydrogen peroxide is obtained as filtrate.

$$BaO_2 + CO_2 + H_2O = BaCO_3 \downarrow + H_2O_2$$

(iii) From sodium peroxide—Merck's perhydrol :

Calculated quantity of *sodium peroxide* is added to *dilute (20%) sulphuric acid* cooled to 0°C placing it in a freezing mixture of ice and common salt. The acid reacts with Na_2O_2 with the formation of sodium sulphate and hydrogen peroxide. At a low temperature sodium sulphate separates out as *crystalline Glauber's salt* (Na_2SO_4, $10H_2O$) which is removed by filtration. The aqueous solution of hydrogen peroxide is obtained as filtrate. This aqueous solution on distillation under low pressure yields 30% solution of hydrogen-peroxide.

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$

This 30% solution of hydrogen peroxide is sold in the market under the trade name Merck's perhydrol.

- **Excess of Na_2O_2 is avoided in the preparation of H_2O_2 from Na_2O_2—Explain why.**

In the preparation of H_2O_2 from Na_2O_2, calculated amount of Na_2O_2 should be used. Because excess of Na_2O_2 will react with water to produce NaOH which acts as positive catalyst in the decomposition of H_2O_2.

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$$

1.26. Large scale preparation of hydrogen peroxide.

(1) By electrolytic process :

Hydrogen peroxide is obtained in a large scale by the electrolysis of 50% sulphuric *acid at ice-cold temperature by using copper as cathode and platinum as anode.* On passing electric current *perdisulphuric acid* is produced at the anode. The produced perdisulphuric acid is collected from the anode chamber and reacted with calculated amount of water when perdisulphuric acid is hydrolysed to produce hydrogen peroxide. The dilute solution of hydrogen peroxide thus produced is then subjected to distillation under reduced pressure at 80°C, when 30% hydrogen peroxide is obtained. Higher concentration (90 – 99%) is commercially achieved by multistage fractionation.

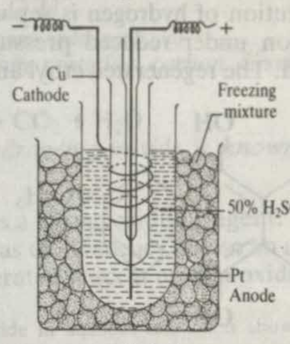


Fig 1.31 :

$$2H_2SO_4 \rightleftharpoons 2H^+ + 2HSO_4^-$$

$$\textit{At cathode}: 2H^+ + 2e = H_2 \uparrow$$

$$\textit{At anode}: 2HSO_4^- - 2e = 2HSO_4$$

$$2HSO_4 \rightarrow H_2S_2O_8 \text{ (perdisulphuric acid)}$$

$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2$$

[Although the formation of H_2O_2 involves the formation of $H_2S_2O_8$ and subsequent hydrolysis, the possibility of formation of per mono sulphuric acid and subsequent hydrolysis can not be ruled out.

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$$

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2]$$

Thus sulphuric acid is regenerated which can be electrolysed again to produce more H_2O_2.

[Alternatively the electrolysis may be carried out with ammonium hydrogen sulphate [$(NH_4)_2SO_4$ + H_2SO_4] using Cu coil as cathode and platinum wire as anode. In this case ammonium per sulphate is liberated at the anode which is collected and distilled with dil. H_2SO_4 under pressure when hydrogen peroxide is produced.

$$NH_4HSO_4 \rightleftharpoons H^+ + NH_4SO_4$$

$$\textit{At cathode}: 2H^+ + 2e \rightarrow H_2$$

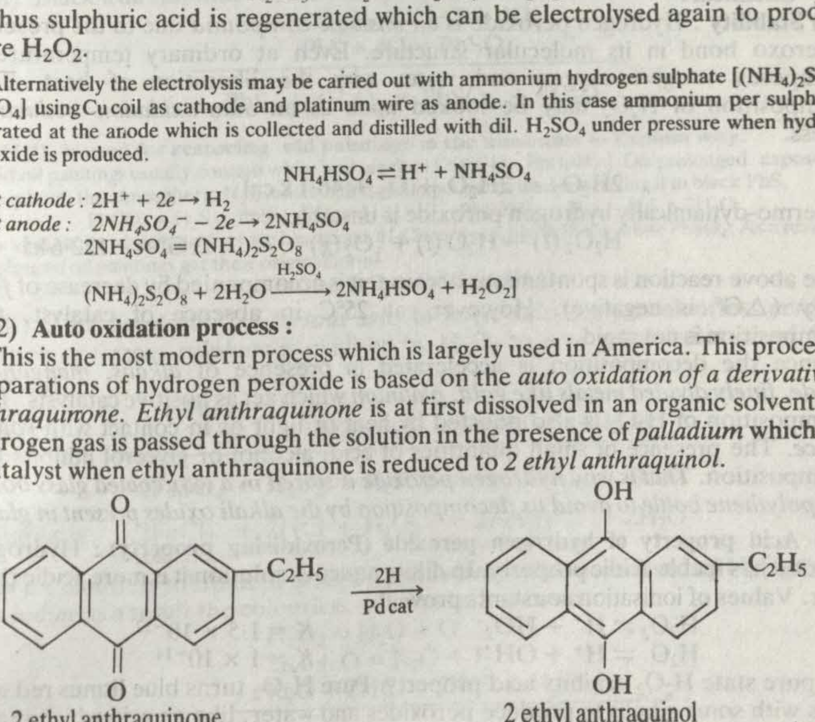
$$\textit{At anode}: 2NH_4SO_4^- - 2e \rightarrow 2NH_4SO_4$$

$$2NH_4SO_4 = (NH_4)_2S_2O_8$$

$$(NH_4)_2S_2O_8 + 2H_2O \xrightarrow{H_2SO_4} 2NH_4HSO_4 + H_2O_2]$$

(2) **Auto oxidation process :**

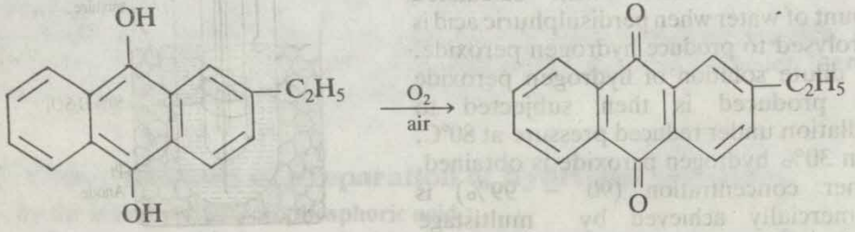
This is the most modern process which is largely used in America. This process of preparations of hydrogen peroxide is based on the *auto oxidation of a derivative of anthraquinone. Ethyl anthraquinone* is at first dissolved in an organic solvent and hydrogen gas is passed through the solution in the presence of *palladium* which acts a catalyst when ethyl anthraquinone is reduced to *2 ethyl anthraquinol.*



2 ethyl anthraquinone

2 ethyl anthraquinol

In the next step, 2 ethyl anthraquinol thus produced is oxidised by passing air through the solution when 2 ethyl anthraquinol is oxidised to 2 ethyl anthraquinone with the formation of hydrogen peroxide. The mixture is shaken with water when 20% solution of hydrogen is separated. The H_2O_2 thus obtained is subjected to distillation under reduced pressure when a concentrated solution of H_2O_2 is obtained. The regenerated ethyl anthraquinone can be used again.



The continuity of the process is thus maintâined. This process needs only H_2, air and water as the major raw materials.

1.27. Properties of hydrogen peroxide.

[A] **Physical :** (i) Anhydrous hydrogen peroxide is a colourless syrupy liquid having an odour resembling that of nitric acid. In thick layers it gives blue tinge. It is soluble in water as well as in organic solvents like alcohol, ether etc. (v) Its density is 1.46 g/cc. at 0°C and its boiling point is 151°C.

[B] **Chemical :**

(1) **Stability :** Hydrogen peroxide is *an unstable compound* due to the presence of peroxo bond in its molecular structure. Even at ordinary temperature it decomposes to give oxygen and water with the liberation of heat. The decomposition of H_2O_2 may be looked upon as an *auto-oxidation- reduction* process.

$$2H_2\overset{-1}{O}_2 = 2H_2\overset{-2}{O} + \overset{0}{O}_2 + 46{\cdot}1\ \text{k cal}$$

Thermo-dynamically hydrogen peroxide is unstable.

$$H_2O_2\,(l) \rightarrow H_2O\,(l) + \tfrac{1}{2}O_2\,(g) \qquad \Delta G^\circ = -122{\cdot}6\ \text{kJ}$$

The above reaction is spontaneous because, it is accompanied by decrease of *free energy* (ΔG° is negative). However, at 25°C in absence of catalyst, the decomposition is not rapid.

Hence the decomposition is accelerated in presence of *alkalis, manganese dioxide, finely divided metals like gold, platinum* which act as positive catalysts. The decomposition of H_2O_2 is also boosted by heat or light or in contact with *rough surface.* The presence of small quantities of acid, alcohol or glycerol inhibits the decomposition. *That is why hydrogen peroxide is stored in a wax coated glass bottle or in polythene bottle to avoid its decomposition by the alkali oxides present in glass.*

(2) **Acid property of hydrogen peroxide (Peroxidising property) :** Hydrogen peroxide has feeble acidic property. In dilute aqueous solution it is more acidic than water. Values of ionisation constants prove it.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad K = 1{\cdot}5 \times 10^{-12}$$
$$H_2O \rightleftharpoons H^+ + OH^- \qquad K = 1 \times 10^{-14}$$

In pure state H_2O_2 exhibits acid property. Pure H_2O_2 turns blue litmus red and reacts with some alkalis to produce peroxides and water, like an acid which reacts with alkalis to form salt and water. It reacts with *sodium hydroxide, potassium hydroxide, ammonia and barium hydroxide* to form the corresponding peroxides.

$$2NaOH + H_2O_2 = Na_2O_2 + 2H_2O\ ; \qquad Ba(OH)_2 + H_2O_2 = BaO_2 + 2H_2O$$

$$\underset{\text{(ammonium hydro peroxide)}}{NH_3 + H_2O_2 = NH_4O_2H}$$

It reacts with *sodium carbonate* to give *sodium peroxide, carbon dioxide* and *water.*

$$Na_2CO_3 + H_2O_2 = Na_2O_2 + CO_2 + H_2O$$

This property of producing peroxides by hydrogen peroxide is known as its peroxidising property.

(3) **Oxidising property :** Hydrogen peroxide is a strong oxidising agent. Due to the presence of peroxo-bond in its molecule, it has the tendency to lose an atom of nascent oxygen ($H_2O_2 = H_2O + O$) and the liberated nascent oxygen oxidises the others.

[The oxidation-reduction chemistry of hydrogen peroxide in aqueous solution is shown in the following potentials.

$$\begin{array}{ll} H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O & E^\circ = 1{\cdot}77 \text{ volt} \\ O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2 & E^\circ = 0{\cdot}68 \text{ volt} \\ HO_2^- + H_2O + e \rightleftharpoons 3OH & E^\circ = 0{\cdot}87 \text{ volt} \end{array}$$

The above standard reduction potential values show that H_2O_2 is a strong oxidising agent either in acid or in alkali solution i.e., irrespective of pH of the solution. Only towards very strong oxidising agents e.g., MnO_4^-, it can act as a reducing agent. The oxidising action of H_2O_2 in acid medium is slow where as in alkali medium its oxidising action is fast.]

(i) Hydrogen peroxide *sets fire* to a mixture of *magnesium powder and manganese dioxide.*

(ii) *Black lead sulphide* is oxidised by H_2O_2 to form *white lead sulphate.*

$$\begin{array}{c} 4H_2O_2 = 4H_2O + 4O \\ PbS + 4O = PbSO_4 \\ \hline \overset{-2}{PbS} + 4H_2O_2 = Pb\overset{+6}{S}O_4 + 4H_2O \end{array}$$

• H_2O_2 is used for restoring old paintings in the museums —Explain why.

Old oil paintings usually contain white lead pigment [$2PbCO_3, Pb(OH)_2$]. On prolonged exposure to atmosphere, the atmospheric H_2S reacts with this compound of lead converting it to black PbS.

$$PbCO_3 + H_2S = PbS + CO_2 + H_2O\ ; \qquad Pb(OH)_2 + H_2S = PbS + 2H_2O$$

As a result the white paintings are blackened. H_2O_2 converts black PbS to white $PbSO_4$. As a result the discoloured oil paintings get their original form.

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

(iii) It oxidises *acidified ferrous salts* to *ferric salts* e.g., a colourless *acidified solution of ferrous sulphate* is oxidised by H_2O_2 to give yellow solution of *ferric sulphate.*

$$\begin{array}{c} H_2O_2 = H_2O + O \\ 2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O \\ \hline 2\overset{+2}{Fe}SO_4 + H_2O_2 + H_2SO_4 = \overset{+3}{Fe}_2(SO_4)_3 + 2H_2O \end{array}$$

$$\text{Similarly,} \quad \underset{\text{colourless}}{2\overset{+2}{Fe}Cl_2} + 2HCl + H_2O_2 = \underset{\text{yellow}}{2\overset{+3}{Fe}Cl_3} + 2H_2O$$

(iv) Colourless solution of *acidified potassium iodide* is oxidised by H_2O_2 to give *free iodine* as a result the colourless solution turns brown.

$$\begin{array}{c} H_2O_2 = H_2O + O \\ 2KI + O = K_2O + I_2 \\ K_2O + 2HCl = 2KCl + H_2O \\ \hline 2K\overset{-1}{I} + H_2O_2 + 2HCl = 2KCl + \overset{0}{I_2} + 2H_2O \end{array}$$

$$\text{Similarly,} \quad 2NaI + H_2O_2 + 2HCl = 2NaCl + I_2 + 2H_2O$$

(v) It oxidises the *nitrites* to *nitrates*. Thus potassium nitrite is oxidised to potassium nitrate. *Nitrous acid* is oxidised by H_2O_2 to *nitric acid*.

$$H_2O_2 = H_2O + O$$
$$KNO_2 + O = KNO_3$$
$$K\overset{+3}{N}O_2 + H_2O_2 = K\overset{+5}{N}O_3 + H_2O$$
$$H\overset{+3}{N}O_2 + H_2O_2 = H\overset{+5}{N}O_3 + H_2O$$

(vi) *Sulphurous acid* and *sulphites* are oxidised to *sulphuric acid* and *sulphates* respectively.

$$H_2\overset{+4}{S}O_3 + H_2O_2 = H_2\overset{+6}{S}O_4 + H_2O$$
$$Na_2SO_3 + H_2O_2 = Na_2SO_4 + H_2O$$

(vii) An *acidified solution of potassium ferrocyanide* is oxidised to produce *potassium ferricyanide.*

$$H_2O_2 = H_2O + O$$
$$2K_4[Fe(CN)_6] + O = 2K_3[Fe(CN)_6] + K_2O$$
$$K_2O + 2HCl = 2KCl + H_2O$$
$$2K_4[\overset{+2}{Fe}(CN)_6] + H_2O_2 + 2HCl = 2KCl + 2K_3[\overset{+3}{Fe}(CN)_6] + 2H_2O$$

(viii) *Hydrogen sulphide* is oxidised to free *sulphur.*

$$H_2\overset{-2}{S} + H_2O_2 = \overset{0}{S}\downarrow + 2H_2O$$

(ix) It oxidises acidified *stannous chloride* to *stannic chloride.*

$$\overset{+2}{Sn}Cl_2 + 2HCl + H_2O_2 = \overset{+4}{Sn}Cl_4 + 2H_2O$$

Hydrogen peroxide is reduced to water in all the reactions illustrated above.

(4) **Reducing property :** Towards *strong oxidising agents* hydrogen peroxide can act as a reducing agent.

(i) In *alkaline solution, silver oxide* is reduced by hydrogen peroxide to *metallic silver.*

$$\overset{+1}{Ag_2}O + H_2O_2 = 2\overset{0}{Ag} + H_2O + O_2$$

(ii) It reduces *lead dioxide* to *lead monoxide.*

$$PbO_2 + H_2O_2 = PbO + H_2O + O_2$$

(iii) *Hydrogen peroxide reduces ozone to oxygen, chlorine to hydrochloric acid, bromine to hydrobromic acid.*

$$O_3 + H_2O_2 = 2O_2 + H_2O \;;\quad Cl_2 + H_2O_2 = 2HCl + O_2$$

(iv) *Acidified solutions of potassium permanganate* is reduced to *colourless manganous salt.* Thus the pink colour of the solution turns colourless.

$$2KMnO_4 = K_2O + 2MnO + 5O$$
$$5H_2O_2 + 5O = 5H_2O + 5O_2$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O$$
$$2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O$$
$$2K\overset{+7}{Mn}O_4 + 5H_2\overset{-1}{O_2} + 3H_2SO_4 = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 5\overset{0}{O_2} + 8H_2O$$

[In this reaction the oxidation number of Mn in $KMnO_4$ has been decreased from +7 to +2. So it is reduced. On the other hand the oxidation number of oxygen in H_2O_2 has been increased from −1 to 0. It is therefore oxidised. Thus it is a redox reaction.]

(v) *Sodium hypobromite* or *potassium hypobromite* is reduced by H_2O_2 to give the corresponding *bromides.*

$$NaO\overset{+1}{Br} + H_2O_2 = Na\overset{-1}{Br} + H_2O + O_2$$

(vi) Bleaching powder is reduced to give *calcium chloride* with the evolution of *oxygen*.

$$Ca(OCl)Cl+H_2O_2=CaCl_2+H_2O+O_2$$

(vii) Alkaline solution of *potassium ferricyanide* is reduced to *potassium ferro cyanide* by H_2O_2.

$$2K_3[\overset{+3}{Fe}(CN)_6]+2KOH+H_2O_2=2K_4[\overset{+2}{Fe}(CN)_6]+2H_2O+O_2$$

(viii) Orange coloured acidified *potassium dichromate* solution is reduced to green solution due to the formation of *chromic salt*. In the first step, acidified $K_2Cr_2O_7$ reacts with hydrogen peroxide to form *perchromic acid* (CrO_5). In the second step, the produced perchromic acid reacts with H_2SO_4 to form chromic salt.

(a)

$$\begin{array}{l} K_2Cr_2O_7 + H_2SO_4 = H_2Cr_2O_7 + K_2SO_4 \\ H_2Cr_2O_7 + 4H_2O_2 = 2CrO_5 + 5H_2O \\ \hline K_2Cr_2O_7+H_2SO_4+4H_2O_2 = 2CrO_5+K_2SO_4+5H_2O \end{array}$$

(b)

$$4CrO_5 + 6H_2SO_4 = \underset{\text{(green)}}{2Cr_2(SO_4)_3} + 7O_2 + 6H_2O$$

(c) Acidified MnO_2 is reduced to manganous salt by H_2O_2.

$$\overset{+4}{Mn}O_2 + H_2SO_4 + H_2O_2 = \overset{+2}{Mn}SO_4 + 2H_2O + O_2$$

[In the above reactions H_2O_2 appears to behave as a reducing agent. A reducing agent reduces, only when it is oxidised. But in all the above reactions H_2O_2 is not oxidised. Practically by losing one atom of oxygen, it is reduced to water. The oxygen atom thus liberated from H_2O_2 combines with one atom of oxygen which comes from the other reactant to form a molecule of oxygen.

$$\begin{array}{c} H_2O_2 = H_2O + O \\ Ag_2O + O = 2Ag + O_2 \\ \hline Ag_2O + H_2O_2 = 2Ag + O_2 + H_2O \end{array}$$

According to the electronic concept of oxidation and reduction it can be shown that H_2O_2 can act as reducing agent. During reducing action H_2O_2 loses electrons and gives one molecule of oxygen. The peroxide ion (O_2^{2-}) of H_2O_2 gives electrons and thus oxidised to O_2, and the electrons left by peroxide ion, are accepted other atoms or ions and thus they are reduced, e.g., In the reaction of H_2O_2 with chlorine, the electrons left by the peroxide ion of H_2O_2 are accepted by Cl_2 to form Cl^- ions which combine with the H^+ of H_2O_2 to from HCl and thus Cl_2 is reduced,

$$\begin{array}{l} H_2O_2 \rightleftharpoons 2H^+ + O_2^{2-} \\ O^{2-}_2 - 2e \rightarrow O_2 \text{ (oxidation)} \\ Cl_2 + 2e \rightleftharpoons 2Cl^- \text{ (reduction)} \\ 2H^+ + 2Cl^- = 2HCl] \end{array}$$

• Hydrogen peroxide can act both as an oxidising and a reducing agent—Explain.

In the light of the oxidation number it can be shown that hydrogen peroxide can act both as an oxidising agent and a reducing agent. The oxidation number of oxygen atom in hydrogen peroxide is -1, which lies between the oxidation number of oxygen atom in H_2O i.e., (-2) and that of free oxygen, i.e., (0). Thus the oxygen atom in H_2O_2 may have the tendency to decrease its oxidation number from (-1) to (-2) to form water or it may have the tendency to increase its oxidation number from (-1) to (0) and thus to convert into free oxygen.

(i) When the oxidation number of oxygen in H_2O_2 is increased from (-1) to (0) it is oxidised and this oxidation is carried out at the cost of reducing the others. Under this condition H_2O_2 acts as a reducing agent. Thus Ag_2O is reduced by H_2O_2 to form metallic silver, itself being oxidised to oxygen.

$$\overset{+1}{Ag_2}O + H_2\overset{-1}{O_2} = 2\overset{0}{Ag} + H_2O + \overset{0}{O_2}$$

(ii) When the oxidation number of oxygen atom in H_2O_2 is decreased from (-1) to (-2), it is reduced and this reduction is carried out at the cost of oxidising the others. Thus under this condition H_2O_2 exhibits oxidation property e.g., PbS, is oxidised by H_2O_2 to form $PbSO_4$, H_2O_2 being reduced to water.

$$Pb\overset{-2}{S} + 4H_2\overset{-1}{O_2} = Pb\overset{+6}{S}O_4 + 4H_2\overset{-2}{O}$$

(5) **Bleaching property :** Hydrogen peroxide can bleach silk, wool, ivory etc. H_2O_2 decomposes at first to give off nascent oxygen and this nascent oxygen bleaches the colouring matters by oxidation.

$$H_2O_2 = H_2O + O$$

$$\text{Coloured matters} \xrightarrow{[O]} \text{bleached substance.}$$

(6) **Formation of addition compounds :** Hydrogen peroxide forms addition compounds with some inorganic salts, like water that forms hydrates. It also forms some addition compounds with few organic compounds. Thus it forms addition-compounds with *potassium fluoride* [KF, H_2O_2], *ammonium sulphate* [$(NH_4)_2SO_4, H_2O_2$]. With *urea* it forms [$CO(NH_2)_2, H_2O_2$].

- **Tests of hydrogen peroxide :**

(i) Hydrogen peroxide liberates free *iodine* when treated with an *acidified solution of KI or NaI*. Starch when comes in contact with this free iodine turns blue.

$$2KI + 2HCl + H_2O_2 = 2\,KCl + I_2 + 2H_2O$$

$$I_2 + \text{Starch} \rightarrow \text{blue substance}$$

(ii) **Perchromic acid test :** When H_2O_2 is shaken *with an acidified solution of potassium dichromate with little ether*, the ether layer turns blue. The blue colour is due to the formation of *perchromic acid*.

$$K_2Cr_2O_7 + H_2SO_4 = H_2Cr_2O_7 + K_2SO_4$$

$$H_2Cr_2O_7 + 4H_2O_2 = \underset{\text{Perchromic acid}}{2CrO_5} + 5H_2O$$

The blue colour turns green as the produced *perchromic acid* is converted into *chromic sulphate*.

$$4CrO_5 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 7O_2 + 6H_2O$$

(iii) When few drops of H_2O_2 are added to *titanium sulphate* solution, the *colourless solution turns orange red* in slightly acid medium. The solution on being diluted converts to yellow. The colour is probably due to the formation of *pertitanic acid* ($TiO_3, n\,H_2O$).

$$Ti(SO_4)_2 + 2H_2O_2 = TiO_3 + 2H_2SO_4 + 1/2\,O_2$$

According to some, the orange colour is due to the formation of *per oxo-disulphato-titanic acid.*

$$Ti(SO_4)_2 + H_2O_2 = H_2[TiO_2(SO_4)_2]$$

- **Strength of hydrogen peroxide :**

The strength of a sample of hydrogen peroxide solution is generally expressed *in terms of volume.*

The strength of H_2O_2 in volume, is the volume of oxygen in cm^3 at N.T.P. which is evolved by the decomposition of one cm^3 of hydrogen peroxide solution by the application of heat or by contact with a catalyst.

Thus by *'20 volumes hydrogen peroxide'*—means that when 1 volume of this solution of H_2O_2 is heated, it will give 20 volumes of oxygen at N.T.P. *'x volumes hydrogen peroxide'*—means that when 1 ml of this sample is decomposed by heating, it liberates x ml of O_2 at N.T.P. Thus, 10 ml of *'20 volumes'* hydrogen peroxide will give on heating $10 \times 20 = 200$ ml of O_2 at N.T.P.

(a) *Conversion of volume strength to percentage strength :*

$$\underset{68\,g}{2H_2O_2} = 2H_2O + \underset{\substack{22400\,ml\\ at\,N.T.P.}}{O_2}$$

From the above equation we get,

68 g of H_2O_2 liberate 22400 ml of O_2 at N.T.P.

$\therefore$ 1 g of H_2O_2 liberates $\frac{22400}{68}$ ml = 329·4 ml of O_2 of N.T.P.

Now the solution which contains 1 g of H_2O_2 per 100 ml, the percentage strength is 1%.

i.e., 100 ml of 1% solution of H_2O_2 liberates 329·4 ml of O_2 at N.T.P.

$\therefore$ 1 ml of 1% solution of H_2O_2 liberates $\frac{329 \cdot 4}{100} = 3 \cdot 294$ ml of O_2 at N.T.P.

So 1% H_2O_2 solution = 3·294 volume strength.

3·294 volume strength of H_2O_2 is 1% strength

$\therefore$ 1 volume strength of H_2O_2 is $\frac{1}{3 \cdot 294}$% strength

x volume strength of H_2O_2 is $\frac{x}{3 \cdot 294} = 0 \cdot 3036x$ % strength.

Thus, *when the strength of H_2O_2 solution is expressed in volume strength, the strength can be converted into percentage strength simply by multiplying it by 0·3036.*

(b) *The relation between volume strength of H_2O_2 solution and its strength in terms of normality :*

The equivalent weight $H_2O_2 = \frac{34}{2} = 17$.

68 g of H_2O_2 liberate 22400 ml of O_2 at N.T.P.

$\therefore$ 17 g of H_2O_2 liberate $\frac{22400 \times 17}{68}$ ml = 5600 ml of O_2 at N.T.P.

Now when 17 g of H_2O_2 are present in 1000 ml solution, the strength is 1(N).

$\therefore$ 1000 ml of 1(N) H_2O_2 solution liberate 5600 ml of O_2 at N.T.P.

1 ml of 1(N) H_2O_2 solution liberates $\frac{5600}{1000} = 5 \cdot 6$ ml of O_2 at N.T.P.

Thus, 1(N) H_2O_2 solution = 5·6 volume strength

x(N) H_2O_2 solution = 5·6x volume strength.

Thus the strength of H_2O_2 solution expressed in terms of normality, when multiplied by 5·6, we get the volume strength of the solution.

- **Some typical problems of the strength of H_2O_2 solution.**

1. *Express the strength of '10 volume' H_2O_2 solution is terms of (i) normality, (ii) g/litre and (iii) percentage strength.* [*W.B.J.E.E. '90, M.L.N.R. '90*]

Ans : $$\underset{(68\,g)}{2H_2O_2} = 2H_2O + \underset{(22400\,ml\,at\,N.T.P.)}{O_2}$$

According to the definition—

10 ml of O_2 at N.T.P. are liberated from 1 ml of 10 volume H_2O_2 solution.

$\therefore$ 22400 ml of O_2 at N.T.P are liberated from $\frac{22400}{10}$ ml = 2240 ml of 10 volume solution.

$\therefore$ 2240 ml of H_2O_2 solution contains 68 g of H_2O_2

1000 ml of H_2O_2 solution contain $\frac{68 \times 1000}{2240}$ g = 30·35 g of H_2O_2

(ii) So the strength of 10 volume H_2O_2 solution in terms of g/litre = 30·35.

(i) The equivalent weight of $H_2O_2 = \frac{34}{2} = 17$.

∴ The strength of 10 volume H_2O_2 solution in terms of normality = $\frac{30\cdot35}{17} = 1\cdot785$(N).

(iii) In 1000 ml solution the amount of H_2O_2 = 30·35 g

∴ ,, 100 ml ,, ,, ,, ,, ,, = $\frac{30\cdot35\times100}{1000}$ g

= 3·035 g

∴ The strength of 10 volume H_2O_2 solution in terms of percentage = 3·035%.

2. *Calculate the volume strength of 6·07% solution of hydrogen peroxide.*

Ans : Given that—

100 ml of H_2O_2 solution contain 6·07 g of H_2O_2

∴ 1 ml of H_2O_2 solution contains $\frac{6\cdot07}{100} = 0\cdot0607$ g of H_2O_2

$$\underset{(68\,g)}{2H_2O_2} = 2H_2O + \underset{(22400\,ml\ at\ N.T.P.)}{O_2}$$

68 g of H_2O_2 give 22400 ml of O_2 at N.T.P.

0·0607 g of H_2O_2 gives $\frac{22400\times0\cdot0607}{68}$ ml of O_2 at N.T.P.

= 19·995 ml = 20 ml (approx)

i.e., 1 ml of H_2O_2 solution liberates 20 ml of O_2 at N.T.P.

∴ The strength of the solution in volume strength = 20 volume.

3. *Calculate the volume strength of 1·5 (N) H_2O_2 solution.*

Ans : The equivalent weight of H_2O_2 = 34/2 = 17

∴ 1 litre of 1·5 (N) H_2O_2 solution contains 1·5 × 17 = 25·5 g of H_2O_2

∴ 1 ml of the same solution contains $\frac{25\cdot5}{1000}$ g = 0·0255 g of H_2O_2

68 g of H_2O_2 liberate 22400 ml of O_2 at N.T.P.

∴ 0·0225 g of H_2O_2 liberates $\frac{22400\times0\cdot0225}{68}$ ml of O_2 = 8·4 ml of O_2 N.T.P.

∴ The volume strength of the solution is 8·4 volume.

4. *Show that 10% H_2O_2 solution is stronger than 10 volume H_2O_2 solution.* [*W.B.J.E.E. '86*]

Ans : 10% H_2O_2 solution means

100 ml of the solution contain 10 g of H_2O_2

$$\underset{(68\,g)}{2H_2O_2} = 2H_2O + \underset{(22400\,ml\ at\ N.T.P.)}{O_2}$$

10 volume H_2O_2 solution means

10 ml of O_2 at N.T.P. is liberated from 1 ml of the solution.

∴ 22400 ml of O_2 at N.T.P. is liberated from 2240 ml of the solution.

Thus 2240 ml of the H_2O_2 solution contain 68 g of H_2O_2

100 ml of the H_2O_2 solution contain $\frac{68\times100}{2240} = 3\cdot036$ g of H_2O_2

Thus we see that,

100 ml of 10% solution contain 10 g of H_2O_2 and 100 ml of 10 volume solution contain 3·036 g of H_2O_2

So, 10% solution of H_2O_2 is stronger than 10 volume H_2O_2 solution.

5. *Calculate the number of moles and weight of H_2O_2 present in 500 ml of '10 volume' H_2O_2. Find the amount of H_2O_2 present in 500 ml of 10 volume of H_2O_2.*

Ans :

$$\underset{2\text{ moles}}{2H_2O_2} = 2H_2O + \underset{\substack{(1\text{ mole i.e.,}\\ 22{\cdot}4\text{ litres at N.T.P.})}}{O_2}$$

Given that—

500 ml of 10 volume H_2O_2 give $10 \times 500 = 5000$ ml = 5 litres of O_2 at N.T.P.

From the above equation we get—

22·4 litres of O_2 at N.T.P. are obtained from 2 moles of H_2O_2

$$5 \text{ litres of } O_2 \text{ at N.T.P. are obtained from } \frac{2 \times 5}{22{\cdot}4} \text{ moles} = 0{\cdot}446 \text{ moles of } H_2O_2$$

So, 0·446 moles of H_2O_2 are present in 500 ml of 10 volume H_2O_2 and the weight of H_2O_2 is $0{\cdot}446 \times 34 = 15{\cdot}16$ g.

6. *Calculate the percentage of H_2O_2 in a sample labelled 10 volume.*

[*Roorkee Eng. '89*]

Ans :

$$\underset{68\text{ g}}{2H_2O_2} = 2H_2O + \underset{\substack{22400\text{ ml}\\ \text{at N.T.P.}}}{O_2}$$

10 ml of O_2 at N.T.P. are evolved from 1 ml of H_2O_2 solution

$$22400 \text{ ml of } O_2 \text{ at N.T.P. are evolved from } \frac{22400}{10} = 2240 \text{ ml}$$

Now, 2240 ml of H_2O_2 solution contains 68 g of H_2O_2

$$1000 \text{ ml of } H_2O_2 \text{ solution contains } \frac{68 \times 1000}{2240} \text{ g of } H_2O_2 = 30{\cdot}357 \text{ g of } H_2O_2$$

1000 ml of H_2O_2 solution contains 30·357 g of H_2O_2

$$\therefore\ 100 \text{ ml of } H_2O_2 \text{ solution contains } \frac{30{\cdot}357 \times 100}{1000} \text{ g of } H_2O_2 = 3{\cdot}0357 \text{ g of } H_2O_2$$

∴ The strength in terms of percentage = 3·0357 %.

7. *Calculate the volume in ml of H_2O_2 solution labelled "10 volume", required to liberate 600 ml of O_2 at 27°C and 1 atmospheric pressure.*

Ans : Let the volume of 600 ml of O_2 at N.T.P. be *V* ml

$$\therefore\ \frac{1 \times V}{273} = \frac{1 \times 600}{300} \quad \text{or, } V = 546 \text{ ml}$$

$$\underset{68\text{ g}}{2H_2O_2} = 2H_2O + \underset{22400\text{ ml}}{O_2}$$

Now 10 ml of O_2 are obtained from 1 ml of H_2O_2

$$\therefore\ 546 \text{ ml of } O_2 \text{ are obtained from } \frac{540}{10} = 54 \text{ ml of } H_2O_2.$$

• Experiments to illustrate some important properties of hydrogen peroxide :

(i) ***Prove that hydrogen peroxide is a strong oxidising agent.***

(a) A piece of filter paper soaked in lead acetate solution is introduced into a jar of H_2S. The paper turns black due to the formation of lead sulphide.

$$Pb(CH_3COO)_2 + H_2S = \underset{\text{(black)}}{PbS\downarrow} + 2CH_3COOH$$

Now hydrogen peroxide is added to this blackened filter paper. It is observed that the black colour disappears and the filter paper turns white again. Thus it is proved that H_2O_2 oxidises lead sulphide converting it to white lead sulphate.

$$Pb\overset{-2}{S} + 4H_2O_2 = Pb\overset{+6}{S}O_4 + 4H_2O$$

(b) A clear solution of potassium iodide is taken in a test tube. The solution is acidified by adding dilute hydrochloric acid. Now hydrogen peroxide is added to this acidified solution when the clear solution turns brown due to the liberation of free iodine. This liberated iodine turns starch paper blue. Thus it is proved that H_2O_2 oxidises colourless potassium iodide to free iodine.

$$2K\overset{-1}{I} + 2HCl + H_2O_2 = 2KCl + \overset{0}{I}_2 + 2H_2O$$

(ii) *Illustrate the reducing property of H_2O_2.*

Pink coloured potassium permanganate solution is taken in a test tube. The solution is acidified by adding dilute H_2SO_4. Now hydrogen peroxide is added to this acidified solution of $KMnO_4$. It is observed that the pink coloured solution becomes colourless and oxygen evolves. This is due to the fact that $KMnO_4$ is reduced by H_2O_2 to form colourless manganous salt i.e., $\overset{+7}{Mn}$ has been reduced to give $\overset{+2}{Mn}$.

$$2K\overset{+7}{Mn}O_4 + 3H_2SO_4 + 5H_2\overset{-1}{O}_2 = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 5\overset{0}{O}_2 + 8H_2O$$

(iii) *Prove that H_2O_2 is an unstable compound and easily decomposes to give off oxygen.*

Hydrogen peroxide is taken in a test tube and a pinch of MnO_2 is added to it. It is observed that a colourless and odourless gas evolves which rekindles a glowing chip of wood. The evolved gas is found to be absorbed by alkaline pyrogallate solution turning the solution brown. Thus it is proved that the evolved gas is O_2 which is produced by the decomposition of H_2O_2.

$$2H_2O_2 = 2H_2O + O_2\uparrow$$

1.28. Uses of hydrogen peroxide.

(i) Hydrogen peroxide has its use in medicine as an antiseptic for washing wounds, teeth and ear.

(ii) It is used in the laboratory as an oxidising agent.

(iii) It is used for bleaching hair, straw, silk and wood.

(iv) It is used as a propellent in submarine and as a fuel in rockets.

(v) It has its use to restore colour of old lead paintings whose white lead [$2PbCO_3$, $Pb(OH)_2$] is blackened due to the formation of black PbS by the action of atmospheric H_2S. Hydrogen peroxide oxidises the black PbS to $PbSO_4$ which is white.

(vi) H_2O_2 is used in the detection of Ti, V and Cr metallic ions with which it forms peroxides of characteristic colours.

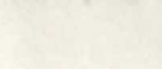
• A mixture of hydrazine and H_2O_2 with Cu (II) catalyst is used as rocket propellant. —Explain why.

The mixture is used as rocket propellant because H_2O_2 reacts with hydrazine in presence of Cu(II) catalyst to produce N_2 and steam. The reaction is highly exothermic and is accompanied by a large increase in volume. This produces an intense pressure which is essential for a rocket.

$$NH_2-NH_2 + 2H_2O_2 \xrightarrow{Cu(II)} N_2(g) + 4H_2O(g) + Heat$$

• Structure of hydrogen peroxide :

The two formulae as suggested for hydrogen peroxide are given below—



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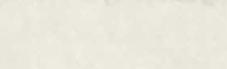
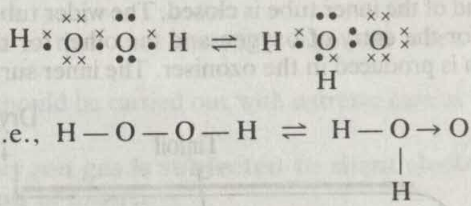
and



Bayer

It has been suggested that hydrogen peroxide molecule is a *tautomeric mixture* of the two forms in its aqueous solution.



$$\mathrm{H\overset{\times}{\cdot}\overset{\times\times}{\underset{\times\times}{O}}\overset{\times}{\cdot}\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}\overset{\times}{\cdot}H \rightleftharpoons H\overset{\times}{\cdot}\underset{H}{\overset{\bullet\bullet}{\underset{\bullet\times}{O}}}\overset{\times}{\cdot}\overset{\times\times}{\underset{\times\times}{O}}\overset{\times}{\cdot}}$$

$$\text{i.e.,}\quad \mathrm{H-O-O-H \rightleftharpoons H-\underset{\underset{H}{|}}{O}\rightarrow O}$$

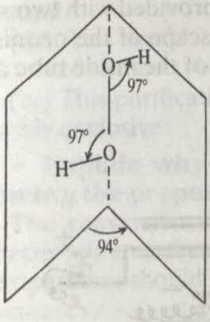


Fig 1.32 : Structure of H_2O_2

All the four atoms in hydrogen peroxide molecule do not lie in the same plane. To have an idea of the structure of hydrogen peroxide molecule consider a book opened at an angle of 94°. The two oxygen atoms are placed at the joining of the two covers, while the two hydrogen atoms are placed one on each cover with H—O—O bond angle = 97°.

OZONE (O_3)

The formation of a new gas by passing electric discharge through air was shown by *Schonbein* in 1840 and he gave the name ozone (I smell) to this new gas. *Soret* and others proved that ozone is an allotrope of oxygen with the molecular formula O_3.

Ozone is present in very small quantities in air near sea side. It is sufficiently present in the ozonosphere of the atmosphere. The presence of ozone in ozonosphere is due to the irradiation of O_2 with U.V. light. Oxygen molecule is activated in the first step and in the following step the activated oxygen molecule and normal O_2 molecule collide to form ozone and atomic oxygen atom.

$$O_2 \xrightarrow{h\nu} O_2^* \quad \text{(activated molecule)}$$

$$O_2^* + O_2 \longrightarrow O_3 + O$$

1.29. Preparation of Ozone.

Ozone is prepared by passing silent electric discharge through pure and dry oxygen.

$$3O_2 \rightleftharpoons 2O_3 \; - \; 241 \text{ k cal}$$

This conversion from oxygen to ozone is a reversible and endothermic reaction. During an ordinary electric discharge much heat and light are generated along with the electric spark. When oxygen is subjected to an ordinary electric discharge, most of the O_3 produced will get decomposed to give O_2 as O_3 is unstable and heat accelerates its decomposition. When any insulating material such as glass, is inserted in the space between the two electrodes and high current density is applied, silent electric discharge passes on between the two electrodes. By this process no spark is produced and much less heat is generated, and as a result the decomposition of the produced ozone is much retarded.

- **Laboratory method of preparation of ozone :**

Ozone is prepared in the laboratory by *passing silent electric discharge through pure and dry oxygen* in an apparatus known as *ozoniser*. Two types of ozonisers are generally used for the preparation of ozone—(i) *Siemen's ozoniser* and (ii) *Brodies ozoniser*.

(i) Preparation of ozone by Siemen's ozoniser :

This apparatus consists of two concentric glass tubes sealed together at one end. The inside end of the inner tube is closed. The wider tube is provided with two side tubes—one for the entry of oxygen and the other for the escape of the ozonised oxygen which is produced in the ozoniser. The inner surface of the inside tube and the outer surface of the outer tube are coated with tin foils. The inner and outer tin foils are connected to the two terminals of an induction coil and a slow stream of pure and dry oxygen is passed through the annular space between the two tubes. Thus the oxygen present in the annular space is subjected to the action of silent electric discharge, when oxygen is partially converted to ozone. Ozonised oxygen comes out of the apparatus from the exit tube and is collected. The ozonised oxygen thus obtained contains 7—10% of ozone.

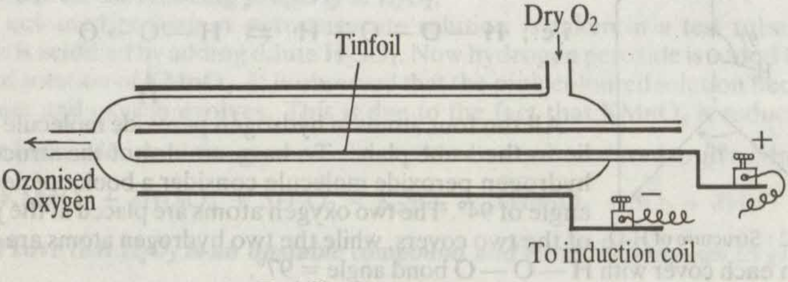


Fig 1.33 : Siemen's ozoniser

(ii) Preparation of ozone by Brodies' apparatus :

Brodies' apparatus consists of two concentric glass tubes. The narrow glass tube, closed at the bottom, is inserted into the wider tube. The narrow tube is sealed at the open end with the wider tube. The narrow tube is filled with dilute sulphuric acid and a platinum electrode is dipped in it. The wider tube is provided with two side tubes—one at the side for the entry of pure and dry oxygen into the apparatus and the other at the bottom for the escape of ozonised oxygen. The whole apparatus is kept immersed in a glass jar which is also filled up with dilute H_2SO_4. A platinum electrode is dipped into the acid solution of the glass jar.

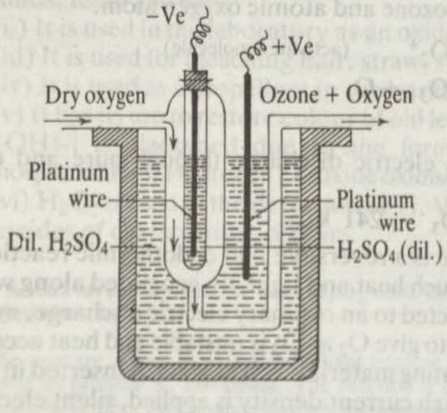


Fig 1.34 : Brodie's apparatus

The two electrodes are now connected to the two terminals of an induction coil and a slow stream of pure and dry oxygen is passed through the annular space between the two tubes. The dry oxygen gas present in the annular space comes under the influence of silent electric discharge and is partially converted to ozone. The ozonised oxygen thus produced comes out of the apparatus through the exit tube and is collected. The ozonised oxygen thus obtained contains about 20% of ozone.

Preparation of pure ozone from ozonised oxygen :

(i) The ozonised oxygen thus obtained is cooled in liquid air when it condenses to give *a deep blue liquid*. This liquid contains liquid oxygen and ozone.

(ii) The blue liquid is then subjected to fractional distillation. As O_2 is more volatile than ozone, evaporates first and is removed by pump. Liquid ozone is left behind.

(iii) This liquid ozone is then very carefully vaporised when pure ozone is obtained as a deep blue gas.

(iv) This purification should be carried out with extreme care as liquid ozone is highly explosive.

- **Explain why—oxygen gas is subjected to silent electric discharge during the preparation of ozone.**

The conversion of oxygen to ozone is a reversible reaction and the forward reaction is endothermic. So according to Le Chatelier's principle, the increase of temperature should favour the forward reaction and thus the yield of ozone should increase.

$$3O_2 \rightleftharpoons 2O_3 - 241 \text{ k cal}$$

But as ozone is very unstable, tends to decompose into oxygen even at room temperature. This decomposition is accelerated by the increase of temperature. During ordinary electric discharge much heat is produced along with the electric spark. If oxygen is subjected to this ordinary electric discharge, the produced ozone will decompose to give oxygen by the generation of heat. If the two electrodes are covered by an insulating material such as glass and are connected to the two terminals of an induction coil, silent electric discharge will occur in between the two electrodes without producing electric spark and heat. When pure oxygen is subjected to this silent electric discharge, the decomposition of the produced ozone is considerably retarded. This is why oxygen is subjected to silent electric discharge for the preparation of ozone.

- **Large scale preparation of ozone.**

Ozonised air is commercially prepared in *Siemen-Halske ozoniser*. It consists of cast iron box having a number of aluminium rods each of which is surrounded by glass or poreclain cylinder. Water is circulated around the glass cylinders to keep the temperature low. The aluminium rods rest vertically on an insulating glass plate and thus the Al rods are kept insulated from the earth-connected iron tank. The aluminium rods are then charged to a high potential of 8000 — 10,000 volts and the iron tank is earthed. The glass cylinders are connected with the earth through the surrounding water and the iron tank. Dry and dust free cold air is passed through an inlet tube at the bottom. It passes through the annular space between the aluminium rods and glass cylinders. Thus the oxygen of air is subjected to the action of silent electric discharge as it rises up through the annular space. The ozonised air passes out from the exit tube at the top.

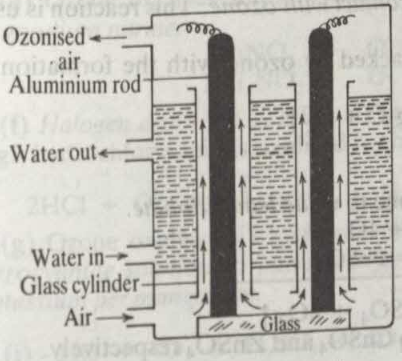


Fig 1.35 : Siemen-Halske ozoniser

1.30. Properties of ozone.

[A] **Physical :** (i) Ozone is pale blue gas having a *fishy smell*. (ii) When condensed, it turns to a dark blue liquid. Liquid ozone is highly explosive. (iii) Its solubility in water is higher than that of oxygen. It is also soluble in organic solvents like carbon tetrachloride, terpentine, acetic acid etc. Due to its high solubility in *terpentine, turpentine is used as an absorber of ozone.*

[B] **Chemical :**

(1) ***Stability :*** When oxygen is converted to ozone, energy is absorbed. Ozone therefore contains more energy than oxygen and consequently it is less stable and much active. Even at ordinary temperature ozone decomposes slowly. Its decomposition becomes rapid at higher temperature (200°C). The decomposition of ozone is catalytically accelerated by finely divided *platinum, silver oxide, manganese dioxide, dust particles* etc. At 300°C ozone is completely decomposed to give O_2.

$$2O_3 \rightleftharpoons 3O_2\text{—Heat}$$

(2) ***Oxidising property :*** As ozone contains more energy than oxygen, *it is more active and vigorous oxidising agent than oxygen.* Its vigorous oxidising action is due to the evolution of nascent oxygen by its spontaneous decomposition even at ordinary temperature. $O_3 = O_2 + O$. This nascent oxygen is responsible for the superior oxidising property of ozone.

There are two classes of oxidation reactions exhibited by ozone.

[A] Reaction in which one molecule of oxygen is given off for every molecule of ozone used in the reaction.

(i) **Oxidation of metals :** Most of the metals are oxidised to their corresponding oxides by ozone.

(a) *Mercury* when comes in contact with ozone at ordinary temperature, is oxidised to give *murcurous oxide.*

$$2Hg + O_3 = Hg_2O + O_2\uparrow$$

Due to the formation of mercurous oxide, *murcury loses its mobility and metallic lustre and sticks to the glass when comes in contact with ozone.* This reaction is used for the identification of ozone.

(b) Metallic silver when warmed, is attacked by ozone with the formation of brown layer of silver oxide.

$$2Ag + O_3 = Ag_2O + O_2\uparrow$$

(ii) **Oxidation of compounds :**

(a) *Black lead sulphide* is oxidised by ozone to *white lead sulphate.*

$$\begin{array}{c} 4O_3 = 4O_2 + 4O \\ PbS + 4O = PbSO_4 \\ \hline Pb\overset{-2}{S} + 4O_3 = Pb\overset{+6}{S}O_4 + 4O_2\uparrow \end{array}$$

Similarly, CuS, ZnS are also converted to $CuSO_4$ and $ZnSO_4$ respectively.

(b) Colourless solution of *acidified ferrous salts* are oxidised by ozone to produce to yellow coloured *ferric salts.*

$$\begin{array}{lllllll} & & O_3 = & O_2 & + O & & \\ 2FeSO_4 & + H_2SO_4 & + O = & Fe_2(SO_4)_3 & + H_2O & & \\ \hline 2\overset{+2}{Fe}SO_4 & + H_2SO_4 & + O_3 = & \overset{+3}{Fe_2}(SO_4)_3 & + O_2 & + H_2O & \\ 2\overset{+2}{Fe}Cl_2 & + O_3 & + 2HCl & = 2\overset{+3}{Fe}Cl_3 & + H_2O & + O_2\uparrow & \end{array}$$

(c) Colourless neutral or acidified solution of *potassium iodide* or *sodium iodide* is oxidised to *free iodine* and the solution turns brown.

$$\begin{array}{c} O_3 = O_2 + O \\ 2KI + O = K_2O + I_2 \\ K_2O + H_2O = 2KOH \\ \hline 2K\overset{-1}{I} + O_3 + H_2O = 2KOH + \overset{0}{I_2} + O_2 \end{array}$$

With acidified solution : $2KI + O_3 + 2HCl = 2KCl + I_2 + O_2 + H_2O$

[It is to be noted that, KI is not oxidised to iodine by ozone in presence of $FeSO_4$. (*Differences from H_2O_2 which can oxidise KI to iodine even in presence of $FeSO_4$*]

(d) Moist *sulphur, phosphorus* and *iodine* are oxidised to their corresponding *higher oxy acids.*

$$\begin{array}{c} (O_3 = O_2 + O) \times 3 \\ S + 3O = SO_3 \\ SO_3 + H_2O = H_2SO_4 \\ \hline \overset{0}{S} + 3O_3 + H_2O = H_2\overset{+6}{S}O_4 + 3O_2 \end{array}$$

$$\begin{array}{c} [O_3 = O_2 + O] \times 5 \\ 2P + 5O = P_2O_5 \\ P_2O_5 + 3H_2O = 2H_3PO_4 \\ \hline 2\overset{0}{P} + 5O_3 + 3H_2O = 2H_3\overset{+5}{P}O_4 + 5O_2 \end{array}$$

$$\begin{array}{c} [O_3 = O_2 + O] \times 5 \\ I_2 + 5O = I_2O_5 \\ I_2O_5 + H_2O = 2HIO_3 \\ \hline \overset{0}{I_2} + 5O_3 + H_2O = 2H\overset{+5}{I}O_3 + 5O_2 \end{array}$$

(e) Ozone oxidises *sodium nitrite* to *sodium nitrate* and *ammonium nitrite* to *ammonium nitrate.*

$$\begin{array}{c} NaNO_2 + O_3 = NaNO_3 + O_2 \\ NH_4NO_2 + O_3 = NH_4NO_3 + O_2 \end{array}$$

(f) *Halogen acids* (HCl, HBr, HI) are oxidised to their corresponding *halogens* e.g., hydrochloric acid is oxidised to chlorine.

$$2H\overset{-1}{Cl} + O_3 = \overset{0}{Cl_2} + O_2 + H_2O \; ; \quad 2H\overset{-1}{Br} + O_3 = \overset{0}{Br_2} + O_2 + H_2O$$

(g) Ozone oxidises (i) *hydrogen sulphide to sulphuric acid* and (ii) *potassium ferrocyanide solution* to *patassium ferricyanide* and (iii) *potassium manganate* to *potassium per manganate.*

(i) $H_2\overset{-2}{S} + 4O_3 = H_2\overset{+6}{S}O_4 + 4O_2$

(ii)
$$\begin{array}{c} O_3 = O_2 + O \\ 2K_4[Fe(CN)_6] + H_2O + O = 2K_3[Fe(CN)_6] + 2KOH \\ \hline 2K_4[\overset{+2}{Fe}(CN)_6] + O_3 + H_2O = 2K_3[\overset{+3}{Fe}(CN)_6] + 2KOH + O_2 \end{array}$$

(iii)
$$\begin{array}{c} O_3 = O_2 + O \\ 2K_2MnO_4 + H_2O + O = 2KMnO_4 + 2KOH \\ \hline 2K_2\overset{+6}{Mn}O_4 + O_3 + H_2O = 2K\overset{+7}{Mn}O_4 + 2KOH + O_2 \end{array}$$

[B] In a few reactions ozone molecule as a whole is used up for oxidation.

Oxygen is not liberated in these reactions.

(a) Ozone oxidises *sulphur di oxide* to *sulphur tri oxide.*

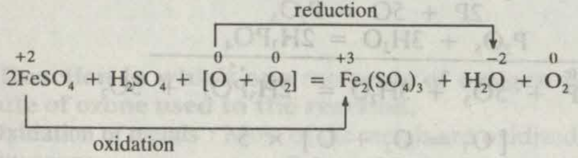
$$3SO_2 + O_3 = 3SO_3$$

(b) Acidified solution of *stannous chloride* is oxidised to *stannic chloride.*

$$3\overset{+2}{Sn}Cl_2 + 6HCl + O_3 = 3\overset{+4}{Sn}Cl_4 + 3H_2O$$

Excepting few reactions, oxygen is evolved in all other oxidation reactions carried out by ozone. As the oxidation number of both ozone and oxygen is zero $[\overset{0}{O}_3, \overset{0}{O}_2]$ it is found that there is no change in the oxidation number of O_3 in the oxidation reactions brought out by ozone. But in a redox reaction the change of oxidation number is a must. As a matter of fact, in the oxidation reactions carried out by ozone, one of the oxygen atom of ozone is reduced by decreasing its oxidation number from zero to (−2). On the other hand, two other oxygen atoms are converted to form free oxygen without changing its oxidation number, i.e. they do not suffer any oxidation or reduction.

Thus in the following oxidation reaction it has been clearly shown that one atom of oxygen of O_3 molecule has brought out the oxidation of $FeSO_4$ itself being reduced to H_2O.

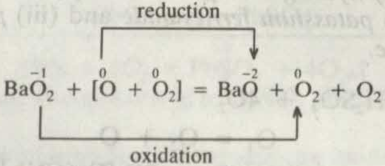


$$2\overset{+2}{Fe}SO_4 + H_2SO_4 + [\overset{0}{O} + \overset{0}{O_2}] = \overset{+3}{Fe_2}(SO_4)_3 + H_2\overset{-2}{O} + \overset{0}{O_2}$$

(3) ***Reactions with peroxides :*** Reaction of ozone with *barium peroxide* and *hydrogen peroxide* results in their mutual reduction with the evolution of oxygen. The *BaO_2 is reduced to BaO* and *H_2O_2 is reduced to H_2O.*

$$BaO_2 + O_3 = BaO + 2O_2$$
$$H_2O_2 + O_3 = H_2O + 2O_2$$

In the reaction with BaO_2 or H_2O_2 the oxygen of the peroxo group is oxidised to free oxygen i.e., the oxidation number of each oxygen atom of the peroxo group of BaO_2 or H_2O_2 is increased from (−1) to zero. On the other hand one atom of oxygen of O_3 is reduced to BaO or H_2O by decreasing its oxidation member from zero to (−2). The oxidation number of remaining two oxygen atoms of O_3 remains unaltered and is liberated as free oxygen.

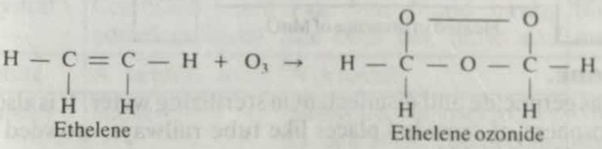


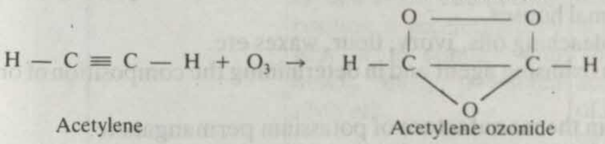
$$Ba\overset{-1}{O_2} + [\overset{0}{O} + \overset{0}{O_2}] = Ba\overset{-2}{O} + \overset{0}{O_2} + O_2$$

As a matter of fact ozone acts as an oxidising agent and H_2O_2 or BaO_2 acts as reducing agent in this reaction. Thus it is proved that *ozone is more powerful oxidising agent than hydrogen peroxide.*

(4) ***Bleaching property :*** The bleaching property of ozone is due to its oxidising property. It liberates nascent oxygen which oxidises indigo and other colouring matters into colourless compounds and thus bleaches them. Litmus paper becomes colourless when exposed to an atmosphere of ozone.

(5) ***Formation of addition compounds :*** With *unsaturated organic compounds* consisting of double or triple bonds, ozone forms addition products called *ozonides.* Thus ozone reacts with *ethelene* to form *ethelene ozonide.*





Rubber contains unsaturation and so it is readily attacked by ozone and as a result the elasticity of rubber is lost.

- **Tests for ozone :**

(i) Ozone is identified by its strong fishy smell.

(ii) A filter paper soaked in KI and starch solution turns blue when brought in contact with ozone. This is due to the fact that ozone first oxidises KI to give free iodine, and this free iodine reacts with starch producing blue colour.

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2$$
$$\text{Starch} + I_2 \rightarrow \text{Turns blue}$$

H_2O_2, Cl_2, NO_2 etc., also respond to this test.

(iii) Ozone turns *benzidine paper brown* and *trimethyl base paper violet.*

(iv) *A drop of mercury when brought in contact with O_3, its mobility and metallic lustre are lost and it sticks to the glass.*

- **Prove that oxygen and ozone are the allotropes of the same element :**

(i) The gaseous ozone is heated in presence of MnO_2 or silver dust when ozone is completely decomposed to give a colourless gas. The product thus obtained by heating ozone, does not change the colour of starch iodide paper to blue. The gas thus obtained is absorbed by alkaline pyrogallate solution turning it brown. Thus it is proved that the gas obtained by the decomposition of ozone is nothing but oxygen.

$$2O_3 = 3O_2$$

(ii) The oxygen thus obtained from ozone is completely dried and taken in a suitable apparatus and subjected to silent electric discharge. The gas coming out of the apparatus is not absorbed by alkaline pyrogallate solution, but a piece of filter paper soaked in potassium iodide and starch solution when brought in contact with this gas turns blue. This proves that the gas coming out of the apparatus is nothing but ozone.

$$3O_2 \xrightarrow{\text{Silent discharge}} 2O_3$$
$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2$$
$$I_2 + \text{Starch} \rightarrow \text{turns blue}$$

Thus it is proved that each of oxygen and ozone can be converted to the other without any change in mass. So it can be concluded that ozone and oxygen are the allotropes of the same element,—the only difference between them is in their molecular structure. Oxygen molecule is diatomic and ozone is triatomic.

$$\boxed{3O_2} \underset{\text{Heated in presence of MnO}_2}{\overset{\text{Silent discharges}}{\rightleftharpoons}} \boxed{2O_3}$$

1.31. Uses of ozone.

(i) Ozone is used as germicide and disinfectant in sterilizing water. It is also used in purifying the atmosphere of crowded places like tube railways, crowded halls, cenema halls and animal houses.

(ii) It is used for bleaching oils, ivory, flour, waxes etc.

(iii) It is used as an oxidising agent and in determining the composition of organic compounds.

(iv) It is also used in the manufacture of potassium permanganate.

(v) It has its use in destroying bad odours that arise from cold storage, big kitchen of hotels and slaughter houses.

• Structure of ozone :

Electron diffraction, microwave spectra show that ozone molecule is angular and the angle between the three oxygen atoms is 116°49′ ± 30′. The O—O bond distance in ozone molecule is 1·278 ± 0·003Å. Since single bond (O−O) distance is 1·49 Å and double bond (O=O) distance is 1·21 Å, it is apparent that the O−O bonds in ozone molecule must have considerable double bond character and the exact structure must be resonance hybrid of the following cannonical forms.

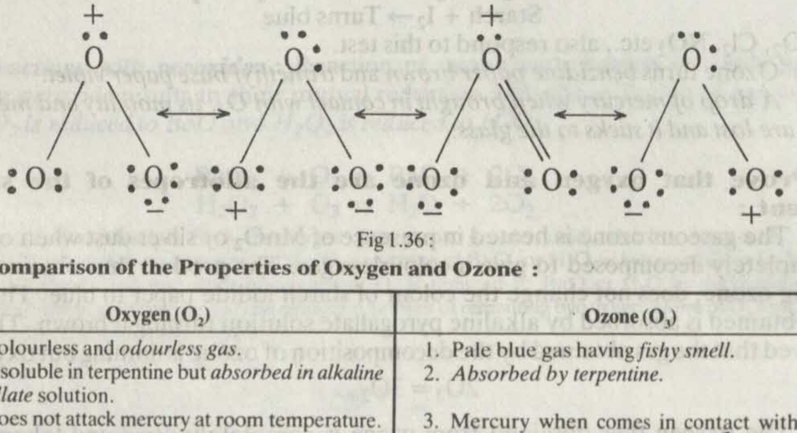


Fig 1.36 :

• Comparison of the Properties of Oxygen and Ozone :

Oxygen (O_2)	Ozone (O_3)
1. Colourless and *odourless gas.*	1. Pale blue gas having *fishy smell.*
2. Insoluble in terpentine but *absorbed in alkaline pyrogallate* solution.	2. *Absorbed by terpentine.*
3. Does not attack mercury at room temperature.	3. Mercury when comes in contact with O_3 at room temperature loses its mobility and metallic lustre due to the formation of Hg_2O. $2Hg + O_3 = Hg_2O + O_2$
4. Stable, but at high temperature decomposes to give nascent oxygen.	4. At 300°C decomposes to give nascent oxygen $O_3 = O_2 + O$. The decomposition is accelerated in presence of MnO_2 or Ag.
5. Does not effect rubber.	5. Attacks rubber at ordinary temperature and as a result rubber loses its elasticity.
6. Can not oxidise PbS to $PbSO_4$.	6. Can oxidise PbS to $PbSO_4$. $PbS + 4O_3 = PbSO_4 + 4\,O_2$
7. Can not oxidises KI solution.	7. Oxidises KI solution liberating free iodine. $2KI + H_2O + O_3 = 2KOH + I_2 + O_2$
8. At 450°C in presence of Pt catalyst SO_2 is oxidised to SO_3.	8. At ordinary temperature SO_2 is oxidised to SO_3.

• Comparison of the properties of water, hydrogen peroxide and ozone :

Property	Water (H_2O)	Hydrogen peroxide (H_2O_2)	Ozone (O_3)
1. Physical State	Colourless and odourless liquid	Pale blue liquid having the smell like nitric acid	Blue gas having a fishy smell
2. Nature	A neutral oxide	A peroxide	An allotrope of oxygen.
3. Stability	Stable	Slowly decomposes to give O_2 and H_2O. The decomposition is accelerated by heat or in contact with MnO_2, dust, powdered silver etc.	Not stable, slowly decomposes to give O_2 at ordinary temperature. The decomposition is accelerated in presence of MnO_2, powdered Ag or Pt.
4. Action on litmus solution	Does not change the colour of litmus	Concentrated solution of H_2O_2 turns blue litmus red	Litmus becomes colourless
5. Action on mercury	Does not react with mercury.	Has no action on mercury	Oxidises mercury to Hg_2O and so mercury loses its mobility and metallic lustre.
6. Oxidising property	Has no oxidising property at ordinary temperature	A powerful oxidising agent. Oxidises KI soln. liberating free I_2. $2KI+2HCl+H_2O_2= 2KCl + I_2 + 2H_2O$	A powerful oxidising agent—oxidises KI soln. liberating free iodine $2KI+H_2O+O_3= 2KOH + I_2 + O_2$
7. Reducing property	Has no reducing property	Reduces acidified $KMnO_4$ soln. to colourless manganous salts	Reaction of ozone with BaO_2 or H_2O_2 results in their mutual reduction with the liberation of O_2
8. Reaction with acidified $KMnO_4$ soln.	Has no action on $KMnO_4$ solution	Reduces $KMnO_4$ to colourless manganous salt.	Does not react with acidified $KMnO_4$ soln.
9. $K_2Cr_2O_7$ soln. + dil. H_2SO_4 + ether	Has no action	The ether layer turns deep blue	Has no action
10. Bleaching property	Has no bleaching property	Bleaches silk, wool, hair etc., by oxidation	Bleaches indigo and vegetable matters by oxidation
11. Formation of addition compounds	Present in salts as water of crystallisation	Forms addition products with many substances e.g., KF, H_2O_2.	Forms addition products with unsaturated organic compounds e.g., ethelene ozonide
12. Action on titanium sulphate soln.	Has no action	Orange yellow colour is produced	Has no action

• Exercise •

1. (a) Describe the laboratory method of preparation of oxygen. (b) What precautions are to be taken during the preparation of oxygen in the laboratory ?

2. How is oxygen gas obtained at ordinary temperature ? How is oxygen obtained from air ? How would you identify oxygen ?

3. Name the gas which is obtained by strongly heated mercuric oxide. Explain why MnO_2 is added to $KClO_3$ in the preparation of oxygen.

4. (a) How would you prove that each of the following compounds contains oxygen—
(i) sodium nitrate, (ii) sulphuric acid, (iii) nitric acid, (iv) barium peroxide.
(b) How would you obtain oxygen from lead nitrate ? *[W.B.H.S. '87]*

5. The word 'oxygen' means 'acid producer'. Give two examples to show that the name given is justified and two other examples to show that the name is a misnomer.
What happens when barium oxide is heated in air ? *[W.B.J.E. '85]*

6. (i) Explain why MnO_2 is added to $KClO_3$ in the preparation of oxygen in the laboratory. Does MnO_2 suffer any change in mass and chemical composition during the reaction ? How would you prove that MnO_2 does not suffer any change in the decomposition of $KClO_3$?

(ii) $KClO_3$ is taken in a hard glass test tube (A) and a mixture of MnO_2 and $KClO_3$ is taken in another test tube (B). The two test tubes are placed vertically side by side on a sand bath and heated.
(a) From which test tube the liberation of O_2 will begin first ?

After the ceasation of the evolution of the gas, water is added to the test tube and the mixture is stirred and filtered.
(b) What is present in the filtrate ?
(c) What is the residue ? What role does it play in the preparation of oxygen ?
(d) How the evolved gas is used for soldering metals ?
(e) Another colourless gas when comes in contact with this gas, a brown coloured gas is produced. What is the brown coloured gas ?
(f) If an iron wire or tar is burnt in oxygen in a sealed tube, will the tube become vacuum ?

7. State conditions under which oxygen reacts with the following—(i) hydrogen, (ii) nitrogen, (iii) sulphur, (iv) phosphorus, (v) sodium, (vi) acidified $FeSO_4$ solution.

8. How would you remove traces of (i) Cl_2 from O_2 *[H.S. '86]*, (ii) NO_2 from O_2, (iii) O_3 from O_2 ?

9. How is hydrogen prepared in the laboratory ? What precautions are to be taken during its preparation ? How is hydrogen purified and collected ? What is nascent hydrogen ? How does it differ from ordinary hydrogen ?

10. How with the help of Kipp's apparatus ready supply of hydrogen gas is obtained in the laboratory ? Explain it with a sketch. *[W.B.H.S. '91, Tr. H.S. '83]*
Illustrate the oxidising action of hydrogen. *[W.B.H.S. '85]*

11. Describe how hydrogen may be obtained by the action of water on (i) a metal at ordinary temperature, (ii) a metal in red hot condition. How can hydrogen be converted into water without using oxygen ? How is hydrogen obtained from nitric acid ? *[W.B.H.S. '88]*

12. Name a metal which when dissolved in hot and concentrated solution of NaOH evolves a colourless gas which burns with a blue flame. *[W.B.J.E.E. '87]*

13. (a) How could you remove traces of (i) nitrogen from hydrogen *[W.B.H.S. '89]*, (ii) oxygen from hydrogen (iii) ozone from hydrogen (iv) moisture from hydrogen ?
(b) Justify that hydrogen can be obtained from (i) alkali, (ii) acid, (iii) water.
(c) Name an element which can liberate hydrogen from cold water. *[W.B.H.S. '83]*

14. (a) What is nascent hydrogen ? *[Tri. H.S. '83, W.B.H.S. '85]*
(b) Describe experiments to prove that—
(i) Hydrogen is lighter than air, (ii) Hydrogen is a reducing agent, (iii) Nascent hydrogen is more powerful reducing agent than ordinary hydrogen. *[W.B.H.S. '86]*

15. Explain the following statements with reasons—
(i) Most metals do not liberate hydrogen by the reaction with nitric acid. *[W.B.H.S. '84, '87]*
(ii) Pure zinc can not be used for the preparation of hydrogen from dil. H_2SO_4. *[W.B.H.S. '85, (Trip.) '82]*
(iii) HNO_3 is not used in the preparation of H_2 by the action of acid on metals. *[Trip. H.S. '83]*
(iv) Hydrogen can not be obtained by the action of a metal on conc. H_2SO_4.
(v) H_2 is liberated by the action of Zn, Mg, or Fe on dil. H_2SO_4 or HCl but H_2 is not liberated when Cu, Ag, Hg are reacted with these acids.
(vi) Hydrogen can act as an oxidising agent.
(vii) Con. HCl is not used in the preparation of H_2 by its action on zinc. *[W.B.H.S. '82]*

(viii) The colour of $FeCl_3$ acidified with HCl remains unchanged when H_2 from Kipp's apparatus is passed through it, but readily becomes colourless when a piece of zinc is added to it. *[I.I.T. '93]*

(ix) Nitric oxide is a neutral oxide but it becomes acidic when comes in contact with air.

(x) Hydrogen may be obtained by the action of a metal on potassium hydroxide.

16. (a) What happens when some bright iron nails are added to potassium permanganate solutions containing dil. H_2SO_4 ? *[W.B.H.S. '90]*

(b) Explain whether the reaction $Fe+HCl=FeCl_3+H_2$ occurs or not.

(c) How can hydrogen be obtained on a large scale from water gas ? *[J.E. '92]*

17. (a) What are hard water and soft water ? *[W.B.H.S. '90]*

(b) Explain why lather is not produced by the action of soap on hard water ? *[W.B.J.E.E. '87]*

(c) Explain the causes of hardness of water. Discuss one method each for removing permanent and temporary hardness of water. *[J.E. '91] [W.B.H.S. '90]*

18. Describe the different processes of removal of hardness of water. How can you obtain as good as distilled water without distillation ?

19. How is the hardness of water measured ? What do you understand by the statement—'The hardness of a sample of tube well-water is 300 ppm ? *[W.B.J.E.E. '87]*

20. Explain with equations how permanent hardness of water is removed by Clark's process. *[W.B.H.S. '81]*

Why is hard water unsuitable for (i) laundry, (ii) boiler *[W.B.H.S. '87]*, (iii) cooking purpose ?

21. (a) What happens when lime is added to permanent hard water ? *[W.B.H.S. '82]*

(b) Which among the following is a sample of hard water and which one is soft ?

(i) Explain solution of dil. hydrochloric acid, (ii) a solution of common salt, (iii) a solution of $ZnSO_4$ whether a solution of $MgSO_4$ will behave as hard water.

22. Describe Duma's experiment on the composition of water by weight. *[Trip. H.S. '83]*

23. How could you determine the volumetric composition of water by analytical method and a synthetic method ?

24. State with equations and the conditions under which water reacts with the following—

(i) Sodium, (ii) Magnesium *[W.B.J.E.E. '87]*, (iii) Iron *[W.B.H.S. '90]* (iv) Carbon *[W.B.H.S. '82, '90]*, (v) Calcium carbide, (vi) Calcium cyanamide, (vii) Sodium peroxide, (viii) Phosphorus pentoxide, (ix) Mixture of red phosphorus and iodine, (x) Sodamide.

25. 'Some chemical reactions do not occur without the presence of water'.—Justify the statement. How would you identify a sample of liquid as water ?

26. (a) 'Water is a universal solvent'.—Justify the statement. *[W.B.J.E.E. '85]*

(b) Describe how de-ionised water can be obtained. *[I.I.T. '83]*

27. A sample of water contains 0·001 mole of $CaCl_2$ in one litre. Determine the hardness of the sample in terms of p.p.m. *[W.B.J.E.E. '87]*

28. (a) Explain why the volume of ice is decreased when melted. *[W.B.J.E.E. '84]*

(b) Explain whether bathing in heavy water is harmful or not ? *[W.B.J.E.E. '92]*

29. How the hardness of water is expressed ?

Determine the hardness of a sample of water which contains 0·001 mole of $MgSO_4$ in one litre of the sample. *[W.B.J.E.E. '84]*

30. (a) Prove that water contains hydrogen and oxygen.

(b) Which of the following metals reacts with dil. HCl, but not with water ?—Ag, Cu, Na, Ni, Ca, Fe. Give reasons for your answer.

31. (a) How would you prepare hydrogen peroxide in the laboratory ? How is it purified ?

(b) Describe the principle in preparing hydrogen peroxide by electrolytic method. *[W.B.J.E. '89]*

(c) Illustrate—(i) the acid property of H_2O_2 *[W.B.J.E.E. '85]*

(ii) the reducing property of hydrogen peroxide. *[W.B.J.E.E. '81]*

32. (a) How is an aqueous solution of H_2O_2 prepared ? How is this aqueous solution of H_2O_2 made concentrated ? *[Tri.H.S. '80]*

(b) How is the strength of H_2O_2 solution expressed ? *[W.B.J.E.E. '85]*

33. During the preparation of H_2O_2 in the laboratory explain why—

(i) a paste of BaO_2 is used instead of anhydrous BaO_2 *[W.B.J.E.E. '85, Trip. H.S. '93]*

(ii) conc. H_2SO_4 or HNO_3 is not used in the preparation of H_2O_2 *[W.B.H.S. '85, '91]*

(iii) at the end of the reaction the final H_2O_2 solution is kept slightly acidic.

(iv) the paste of BaO_2 is added to dil. H_2SO_4 instead of adding the acid to the paste.

(v) HCl is not used in the preparation of H_2O_2.

(vi) syrupy phosphoric acid is preferred to H_2SO_4 in the preparation of H_2O_2 from BaO_2.

34. (i) What is meant by '10 volume' hydrogen peroxide ?

(ii) Why is a small quantity of H_2SO_4 or H_3PO_4 added in a bottle of hydrogen peroxide ? *[W.B.J.E.E. '87]*

(iii) Show that 20% hydrogen peroxide solution is stronger than '20 volume' H_2O_2 solution.

35. (a) Hydrogen peroxide is a weak acid—justify the statement.

(b) What is meant by '10 volume' H_2O_2 ? Express '10 volume' H_2O_2 in percentage strength. Find the amount of H_2O_2 in gram, present in 10 ml of 10 volume H_2O_2. *[W.B.J.E.E. '90]*

(c) Write a balanced equation for a reaction in which H_2O_2 acts as a reducing agent. *[W.B.J.E.E. '90]*

(d) How will you prevent the decomposition of H_2O_2 ? *[Tri. H.S. '85] [W.B.J.E.E. '85]*

36. Illustrate the (a) oxidising property, (b) reducing property, (c) peroxidising property of H_2O_2. *[H.S. '93]*

37. (a) Describe experiments to prove that (i) H_2O_2 is an oxidising agent, (ii) H_2O_2 behaves as a reducing agent *[W.B.J.E.E. '83]* (iii) H_2O_2 behaves as an acid. *[W.B.J.E.E. '83]*

(b) What is Merck's perhydrol ? How is it prepared ?

(c) Give two tests to distinguish between H_2O_2 and H_2O. *[W.B.H.S. '87]*

(d) Indicate the nature of bond present in H_2O_2. *[W.B.J.E.E. '90]*

38. State with reasons why—(i) H_2O_2 acts both as an oxidising and a reducing agent. (ii) MnO_2 is manganese dioxide but BaO_2 is barium peroxide. (iii) H_2O_2 has bleaching property.

39. What happens when (i) MnO_2 is added to H_2O_2 solution, (ii) MnO_2 and H_2SO_4 are added to H_2O_2 solution. What is the role of MnO_2 in these two reactions ?

40. Explain with equations and the changes that takes place when—

(i) H_2O_2 is added to acidified $KMnO_4$ solution. *[W.B.H.S. '85]*

(ii) H_2O_2 is added to an acidified solution of potassium iodide. *[W.B.J.E.E. '85]*

(iii) A filter paper soaked in lead acetate solution and then treated with H_2O_2 solution. *[W.B.H.S. '88]*

(iv) Bromine is treated with an alkaline solution of hydrogen peroxide. *[W.B.J.E.E. '88]*

(v) Potassium di-chromate solution acidified with H_2SO_4 is added to H_2O_2 and the mixture is shaken with ether. *[W.B.J.E.E. '89]*

(vi) H_2O_2 is treated with an alkaline solution of potassium ferricyanide. *[I.I.T. '82, W.B.H.S. '86]*

(vii) H_2O_2 is added to an aqueous solution of H_2S. *[W.B.H.S. '87]*

(viii) H_2O_2 is added to bleaching powder.

(ix) H_2O_2 is added to an acidified solution of potassium ferrocyanide.

(x) H_2O_2 is added to ferrous sulphate solution acidified with H_2SO_4.

(xi) H_2O_2 is treated with ozone. *[W.B.H.S. '83]*

(xii) H_2O_2 is added to potassium dichromate solution acidified with dilute sulphuric acid. *[W.B.H.S. '85]*

(xiii) CO_2 is passed through BaO_2 suspended in water. *[W.B.H.S. '87]*

41. (a) With a neat sketch of the apparatus used describe the preparation of ozone in the laboratory.

(b) Illustrate the oxidising and reducing action of ozone. *[W.B.J.E.E. '85]*

(c) Write the electron dot structure of ozone. *[W.B.J.E.E. '92]*

42. Explain why—

(i) Oxygen is subjected to silent discharges during the preparation of ozone. *[W.B.J.E.E. '89]*

(ii) Colour solution of potassium iodide turns brown on being treated with ozone.

(iii) Oxygen and ozone are basically the same element.

(iv) Ozone is more powerful oxidising agent than oxygen.

(v) The mobility and metallic lustre of mercury is lost when comes in contact with ozone. *[W.B.J.E.E. '91]*

(vi) A paper soaked in starch iodide solution when brought in contact with ozone turns blue.

(vii) Rubber loses its elastic property when comes in contact with ozone.

(viii) Ozone is unstable.

(ix) When fused CaH_2 is electrolysed, H_2 is liberated at the anode. *[I.I.T. '73]*

(x) H_2 gas is evolved more quickly when Zn treated with dil. HCl than with CH_3COOH.

(xi) Hard water is softened before using in boilers. *[I.I.T. '73]*

(xii) Water is liquid while H_2S is a gas at ordinary temperature. *[Roorkee I.I.T. '81]*

(xiii) Water containing Ca^{2+} or Mg^{2+} ions does not produce lathers with soap.

(xiv) Melting and freezing points of D_2O are higher than those of ordinary water.

(xv) H_2O_2 is better oxidising agent than water. *[I.I.T. '86]* To restore the original colour of old oil paintings, H_2O_2 is used. *[W.B.J.E.E. '92]*

(xvi) Parmanent hard water can not be softened by boiling alone. *[W.B.H.S. '94]*

43. What happens when—

(i) Ozone is reacted with stannous chloride solution acidified with HCl. *[W.B.H.S. '86]*

(ii) Ozone gas is passed over mercury contained in glass tube. *[W.B.J.E.E. '90]*

(iii) Ozone is allowed to react with acidic solution of potassium iodide. Does the presence of $FeSO_4$ make any change to the reaction ? *[H.S. '91, W.B.J.E.E. '90]*

(iv) Ozone is passed through litmus solution. [*H.S. '94, W.B.J.E.E. '90*]
(v) Ozone is reacted with ethelene. [*W.B.H.S. '83*]
(vi) Ozone is treated separately with silver powder and hydrogen peroxide. [*W.B.H.S. '80*]

44. (a) Mention two chemical reactions to distinguish between—(i) ozone and H_2O_2 [*W.B.J.E.E. '91*] (ii) oxygen and O_3 [*W.B.J.E.E. '91*] (iii) oxygen and N_2O.

(b) How could you separate—(i) O_2 from a mixture of O_2 and O_3, (ii) O_3 from a mixture of O_2 and O_3, (iii) O_2 from a mixture of N_2O and O_2, (iv) O_2 from a mixture of H_2 and O_2.

45. The mixture of a white solid A and a black solid B on being heated, a white solid C and gas D are produced. B remains unchanged. A on being heated at highter temperature decomposes to give C and D but the reaction becomes slow. C produces a white precipitate E with $AgNO_3$ solution which dissolves in excess of NH_4OH. D when treated with nitric oxide a brown gas F is produced. Identify A, B, C, D, E and F. What is the role of B in this reaction ? Name another substance which can be used instead of B.

46. Indicate whether the following statements are true or false. (i) H_2O_2 is a stable compound. (ii) Hard water is suitable for laundry purpose. (iii) Ozone is an isotope of oxygen. (iv) Hydrogen peroxide is a hydride of oxygen. (v) Hydrogen can oxidise. (vi) A catalyst can influence the rate of a chemical reaction. (vii) Ozone is absorbed by alkaline pyrogallate. (viii) Nascent hydrogen is more active than ordinary hydrogen.

47. 100 ml of a H_2O_2 solution liberate 4 litres of O_2 at N.T.P. Find the volume strength and percentage strength of the H_2O_2 solution. [***Ans.*** 39·9 vol. 12·14%]

48. (a) 50 ml of ozone at N.T.P are passed through 50 ml of '10 volume' H_2O_2 solution. Find the volume strength of the solution after the reaction.

(b) Find the volume of O_2 at N.T.P. that can be obtained by complete decomposition of 30 cc of 20 volume H_2O_2. [***Ans.*** 600 cc] [*W.B.J.E.E. '92*]

49. What volume of oxygen at N.T.P. will be obtained when 30 ml of 20 volume H_2O_2 on being completely decomposed ? [*J.E. '92*]

50. Find the strength of 10 volume hydrogen peroxide in terms of percentage. [*J.E. '90*]

51. Objective type—

(i) The most abandant element in earth's crust is—
(a) silicon, (b) nitrogen, (c) oxygen, (d) hydrogen. [***Ans.*** (c)]

(ii) Oxyacetylene flame gives a temperature of nearly—
(a) 1800°C, (b) 2000°C, (c) 3000°C, (d) 100°C. [***Ans.*** (c)]

(iii) The chemicals used for the preparation of H_2O_2 in laboratory are—
(a) MnO_2 and HCl, (b) BaO_2 and conc. H_2SO_4, (c) PbO_2 + dil. H_2SO_4, (d) BaO_2 and dil. H_2SO_4. [***Ans.*** (d)]

(iv) The decomposition of H_2O_2 is accelerated in presence of—
(a) dil. H_2SO_4, (b) glycerol, (c) MnO_2, (d) H_3PO_4. [***Ans.*** (c)]

(v) Which one can restore the colour of oil painting ?
(a) Chlorine, (b) BaO_2, (c) H_2O_2, (d) PbO_2. [***Ans.*** (c)]

(vi) The presence of H_2O_2 in solution can be detected by—
(a) starch solution, (b) perchromic acid test, (c) Nessler's reagent, (d) ring test. [***Ans.*** (b)]

(vii) H_2O_2 reacts with NaOH to form Na_2O_2. This illustrate that H_2O_2 behaves as—
(a) oxidising agent, (b) an acid, (c) a base, (d) reducing agent. [***Ans.*** (b)]

(viii) Ozone layer is beneficial to life on the surface of the earth because—
(a) it purifies air, (b) causes rain, (c) prevents bacteria of outer space, (d) absorbs harmful U. V. rays. [***Ans.*** (d)]

(ix) The high boiling point of water is due to—
(a) high specific heat of water, (b) low electrical conductivity of water, (c) the presence of hydrogen bonds in water. [***Ans.*** (c)]

(x) Heavy water is obtained by—
(a) evaporation of water for a long time, (b) continuous electrolysis of water, (c) using mass spectrograph. [***Ans.*** (b)]

(xi) H_2 cannot reduce heated—
(a) CuO, (b) Fe_2O_3, (c) Al_2O_3, (d) ZnO. [***Ans.*** (c)] [*O.J.E.E. '80*]

(xii) Temporary hardness of water is generally due to—
(a) presence of deuterium, (b) presence of bicarbonates of Ca, Mg, (c) Presence of earth impurities, (d) presence chlorides of Ca and Mg. [***Ans.*** (b)] [*O.J.E.E. '84*]

(xiii) Percentage of H_2O_2 in 24 volume H_2O_2 is close to—
(a) 7.3, (b) 4.9, (c) 12, (d) 21, (e) none. [***Ans.*** (a)] [*O.U.A.T. '88*]

(xiv) Zn reacts with dil. H_2SO_4 to give H_2 but Cu can not because—
(a) Zn is more electropositive than H_2 and Cu, (b) Cu is more electropositive than Zn and H_2, (c) none of the above. [***Ans.*** (a)] [*O.M.B.B.S. '85*]

(xv) The trade name of sodium hexameta phosphate used in softening water is—
(a) permutit, (b) zeolite, (c) calgon, (d) Tripsa. [***Ans.*** (c)] *[O.M.B.B.S. '87]*

(xvi) Which of the following can absorb large volume of H_2—
(a) finely divided Pt, (b) finely divided nickel, (c) colloidal soln. of Pd, (d) colloidal ferric hydroxide. [***Ans.*** (c)] *[O.M.B.B.S. '88]*

(xvii) Which of the following hydrides is powerful reducing agent ?
(a) HF, (b) LiH, (c) CH_4, (d) NH_3. [***Ans.*** (b)] *[O.M.B.B.S. '90]*

(xviii) The ionisation energy of H_2 is—
(a) much lower than alkali metals, (b) closer to alkali metals, (c) closer to halogens, [***Ans.*** (c)]

(xix) Which of the following exhibits hydrogen bonding—
(a) O, (b) S, (c) Se, (d) Te. [***Ans.*** (a)]

(xx) Ozone acts as a bleaching agent due to—
(a) its oxidising nature, (b) its reducing nature, (c) its dehydrating action, (d) its acidic nature. [***Ans.*** (a)]

(xxi) Oxygen and Ozone are—
(a) isotopes, (b) isomers, (c) isobers, (d) allotropes. [***Ans.*** (d)] *[A.M.B.B.S. '87]*

(xxii) When the same amount of zinc is treated separately with excess of H_2SO_4 and excess of NaOH, the ratio of volumes of hydrogen evolved is—
(a) 1 : 1, (b) 1 : 2, (c) 2 : 1, (d) 9 : 4. [***Ans.*** (a)] *[I.I.T. '79]*

(xxiii) The sum of the number of neutrons and proton in the isotopes of hydrogen is—
(a) 6, (b) 5, (c) 4, (d) 3. [***Ans.*** (b)] *[I.I.T. '86]*

(xxiv) Temporary hardness of water due to $Ca(HCO_3)_2$ can be removed by adding—
(a) $CaCO_3$, (b) $Ca(OH)_2$, (c) HCl, (d) $CaCl_2$. [***Ans.*** (b)] *[I.I.T. '74]*

(xxv) When zeolite is treated with hard water the Na^+ ions are exchanged with—
(a) H^+ ions, (b) Ca^{2+} ions, (c) SO_4^{2-} ions (d) Mg^{2+} ions, (e) OH^- ions. [***Ans.*** (b) (d)] *[I.I.T. '90]*

(xxvi) HCl is added to the following oxides. Which one would give H_2O_2 ? *[I.I.T. '80]*
(a) MnO_2, (b) PbO_2, (c) BaO_2, (d) NO_2. [***Ans.*** (c)]

(xxvii) The oxidation state of most electronegative element in the products of the reaction BaO_2 and dil. H_2SO_4 are—
(a) 0 and − 1, (b) − 1 and − 2, (c) − 2 and 0, (d) −2 and + 1. [***Ans.*** (b)] *[I.I.T. '91]*

(xxviii) The volume strength of 1·5 N H_2O_2 solution is—
(a) 4·8, (b) 8·4, (c) 3, (d) 8. [***Ans.*** (b)] *[I.I.T. '91]*

(xxix) Heavy water is—
(a) H_2O^{18}, (b) D_2O, (c) water at 4°C. [***Ans.*** (b)] *[I.I.T. '93]*

- **Short answer type questions :**

1. *Why ozone is not formed in the lower layer of atmosphere by U.V. rays ?*

Ans. Oxygen in upper atmosphere absorbs energy from U.V. rays from the sun and changes to atomic oxygen. The atomic oxygen thus produced combines with molecular oxygen to form O_3.

$$O_2 \longrightarrow O + O, \qquad O_2 + O \longrightarrow O_3$$

Thus U.V. rays are absorbed in the upper atmosphere by oxygen of air and consequently U.V. rays do not reach lower atmosphere and hence ozone is not formed in the lower layer of atmosphere. This is why ozone is not formed in the lower layer of atmosphere.

2. *Ozone is powerful oxidising agent than oxygen—explain.*

Ans. Ozone is instable at ordinary temperature and easily decomposed to give nascent oxygen which acts as oxidising agent. Thus O_3 oxidises Hg at room temperature to form Hg_2O. On the other hand O_2 is more stable—and decomposes at high temperature with difficulty. Thus O_2 cannot oxidise Hg at ordinary temperature but do so at high temperature. $2Hg + O_2 \longrightarrow 2HgO$

3. *Why oxygen is some what inert at room temperature ?*

Ans. Oxygen is a diatomic gas and the two O atoms are bonded to each other by strong covalent double bond. (bond energy = 490 kJ mole^{-1}). At ordinary temperature the collisions between oxygen molecules are unable to break the strong double bond O = O, consequently it is some what inert in nature at ordinary temperature. At high temperature however sufficient energy is supplied by the collisions to break the double bond and thus O_2 molecule is decomposed to give nacent O which acts'as oxidising agent.

4. *Both the O—O bond in ozone have the same bond length—explain.*

5. *Explain the following :—*

(a) H_2O_2 is used for restoring old painting in museum. *[Roorkee I.I.T. '87]*

(b) Presence of water is avoided in the preparation of H_2O_2 from Na_2O_2.

(c) Which one is more pure—distilled water or deionised water ? Give reasons.

AIR, NITROGEN AND ITS COMPOUNDS

2

• AIR •

The vast envelope of air completely surrounding the earth is termed 'atmoshphere', The early alchemists regarded air as an element. Priestly, Scheele, Lavoisier and Chavendish proved experimentally that air is not an element but a mixture of gases.

2.1. Constituents of air.

• Lavoisier's experiments on the composition of air :

Experiment No. 1.

(i) Lavoisier took a known amount of (4 ounces) pure mercury in a specially prepared glass retort. The long neck of the retort was communicated with a known volume of air in a graduated bell jar kept inverted over mercury in a trough. At the initial stage the mercury level inside and outside the bell jar was same and the volume of air inside the bell jar was carefully noted. (ii) The retort was then heated in a furnace at a temperature near the boiling point of mercury and the changes were carefully noted. Red scales were found floating on the surface of mercury. The volume of air inside the bell jar went on diminishing and the level of mercury gradually rose up in the bell jar. After 12 days no further scales were found to form and the mercury level was found to be steady showing that there was no further diminution in the volume of air inside the bell jar. Lavoisier measured the volume of the residual air when cold and compared it with the original.

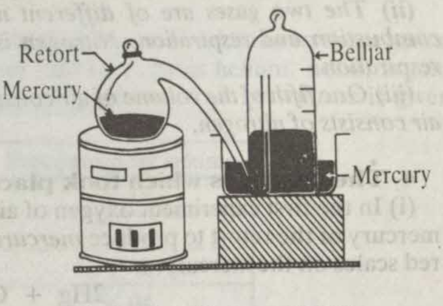


Fig. 2.1 : Lavoisier's experiment

Observation : (i) He observed that diminution in volume was nearly one-fifth of the volume of air originally taken. This is due to the fact that one-fifth of the volume of air originally taken in the bell jar was abosrbed by the heated mercury. (ii) The residual gas in the bell jar was not absorbed by heated mercury. (iii) The residual gas extinguished the flame of a burning candle when introduced in it and a mouse when placed in the gas died due to suffocation.

Inference : From this experiment Lavoisier came to conclusion that the residual gas in the bell jar did not support combustion or respiration. Lavoisier named this gas *'Azote'*. Afterwards this gas was called *nitrogen*.

Experiment—2.

Lavoisier collected the red scales produced in the retort during the first experiment, and placed them in a glass bulb having a long bent delivery tube. The end of the delivery tube was placed under mercury in a trough and a graduated gas jar filled with mercury was inverted over it. He then heated the red scales strongly when a colourless gas was found to evolve which was collected in the graduated gas jar by the downward displacement of mercury. The volume of the gas obtained was found to be equal to the diminution in the volume of air inside the bell jar and the residue left in the glass bulb was mercury. Thus it was found that the volume of air absorbed by mercury in the first experiment was equal to the volume of the gas obtained in the second experiment.

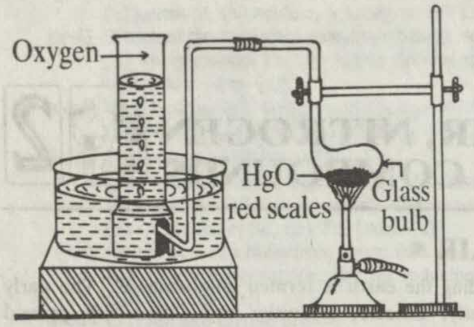


Fig. 2.2 : Lavoisier's experiment No. 2

Lavoisier found that a burning candle continued to burn brilliantly in this gas. He also found that this gas supported respiration.

From the second experiment Lavoisier came to conclusion that the gas obtained from the red scales was a supporter of combustion and respiration. Lavoisier called this gas '*Vital air*' and afterwards named it '*oxygen*'.

From these two experiments Lavoisier came to the conclusion that—

(i) Air is composed of two gases—Oxygen and nitrogen.

(ii) The two gases are of different nature. Oxygen is very active—it supports combustion and respiration. Nitrogen is inert—it does not support combustion or respiration.

(iii) One fifth of the volume of air consists of oxygen and four-fifth of the volume of air consists of nitrogen.

- **The reactions which took place during the experiment.**

(i) In the first experiment oxygen of air inside the bell jar reacted with the heated mercury of the retort to produce *mercuric oxide* which was found to be deposited as red scales on the mercury.

$$2Hg + O = \underset{\text{red scales}}{2HgO}$$

(ii) The red scales i.e., mercuric oxide when heated strongly, decomposed to give *mercury* and *oxygen.*

$$2HgO = 2Hg + O_2\uparrow$$

2.2. Experiment to prove the presence of nitrogen in air.

A piece of white phosphorus is taken in a porcelain crucible. The curcible along with a piece of white phosphorus is allowed to float on water in a glass vessel. A stoppered bell jar is placed over the crucible. The surface of water inside and outside the bell jar is kept in the same level. The volume of air inside the bell jar is divided into five equal parts. Now the stopper is taken out and the phosphorus is ignited by touching it with a hot iron wire. The stopper is quickly replaced. Phosphorus burns giving off a dense white fumes of phosphorus pentoxide. After sometime the burning of phosphorus is stopped. The water level inside the bell jar begins to rise up as the produced phosphorus pentoxide gradually dissolves in water. When the bell jar becomes cold, the level of water inside the bell jar occupies 1/5 th of the volume occupied by air. The remaining gas inside the jar does not support combustion of phosphorus. A burning magnesium ribbon continues to burn in the residual gas in the bell jar with the formation of a white residue. This residue reacts with boiling water with the evolution of ammonia. Thus it is proved that the residual gas inside the bell jar is nitrogen. The reactions that take place.

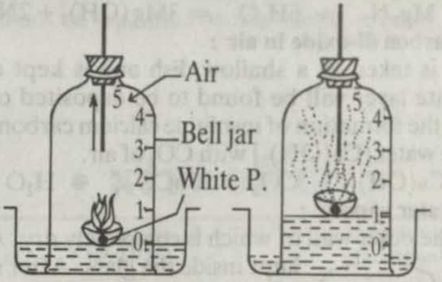


Fig. 2.3 : Presence of nitrogen in air

$P + [O_2 + N_2] \rightarrow P_2O_5 + N_2$

$P_2O_5 + 3H_2O = 2H_3PO_4$ (phosphoric acid)

$3Mg + N_2 = Mg_3N_2$

$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3 \uparrow$

2.3. Composition of air.

The main constituents of air are oxygen and nitrogen. In addition to these gases, air contains carbon di-oxide, water vapour and inert gases helium, neon, argon, krypton, xenon etc in traces. The avarage composition of air by volume is given below—

Constituents	Percentage by volume
Nitrogen	77·16
Oxygen	20·60
Water vapour	1·40
Carbon di oxide	0·04
Inert gases	0·80

Composition of air varies from place to place. Traces of ozone are found to be present on sea side. Besides this, traces of ammonia, carbon monoxide, sulphur di-oxide, hydrogen sulphide are found to present in air of the industrial region.

• Detection of different constituents of air :

(i) Detection of oxygen in air : When a gas jar full of colourless nitric oxide is exposed in air, it is observed that as soon as the nitric oxide of the jar comes in contact with air, brown fumes of nitrogen di-oxide are produced. This is due to the fact that colourless nitric oxide combines with the oxygen of air to form brown fumes of nitrogen dioxide.

$$2NO + O_2 = 2NO_2 \text{ (brown fumes)}$$

(ii) Detection of nitrogen in air :

The residual gas in the bell jar after the removal of oxygen by burning phosphorus, is nitrogen together with water vapour, CO_2 and inert gases. A burning taper extinguished but a burning magnesium ribbon continues to burn in it producing a white product which on treatment with boiling water gives off ammonia. Thus it is proved that the residual gas in the gas jar is nitrogen.

$$3Mg + N_2 = Mg_3N_2$$
$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3\uparrow$$

(iii) **Detection of carbon di-oxide in air :**

Clear lime water is taken in a shallow dish and is kept exposed in air. After sometime a thin white layer will be found to be deposited on the surface of lime water. This is due to the formation of insoluble calcium carbonate which is produced by the action of lime water [$Ca(OH)_2$] with CO_2 of air.

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O\uparrow$$

(iv) **Detection of water vapour :**

A glass is taken, the outer wall of which is completely dry. A few pieces of ice are kept inside the glass. After sometime small drops of colourless liquid are found to form on the outer surface of the glass. This colourless liquid turns white anhydrous copper sulphate blue. Thus, it is proved that the colourless liquid deposited on the outer surface of the glass is nothing but water. The water vapour present in air gets condensed when comes in contact with the cold surface of the glass and thus small drops of water are produced.

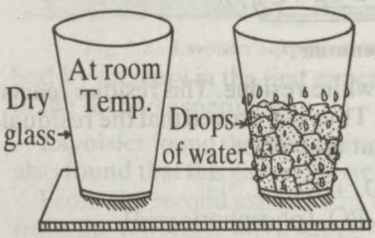


Fig. 2.4 :

2.4. Air is a mechanical mixture and not a chemical compound :

The following evidences prove that air is a mixture of gases and not a compound.

(i) Chemical combination of gases always accompanied by a thermal change and a change in volume. When nitrogen and oxygen are mixed together in the proportions in which they are present is air, no change in volume or temperature takes place. The mixture thus produced behaves like air. If air were a compound there would be a thermal change during its production from its constituents. So air is not a chemical compound.

(ii) A chemical compound is always produced by the combination of two or more elements in definite proportions by weight. But the proportions of the nitrogen and oxygen in air by weight is not exactly constant. Slight variations are observed in samples of air collected from different localities. No compound is found to have a slight variation in its composition.

(iii) The relative density of air is 14·4 which corresponds to a mixture roughly of 4 volumes of nitrogen and 1 volume of oxygen. If air were a compound its formula would have been N_4O or more accurately $N_{15}O_4$ and its relative density would be 36 or 137. But its actual density is 14·4. Thus it is proved that air is not a compound but a mixture.

(iv) As air is a mechanical mixture, its constituents can be separated by easy mechanical methods—

(a) *By fractional distillation :* Liquid air on evaporation, more volatile nitrogen evoporates out first leaving behind almost pure oxygen which is less volatile than nitrogen. If air were a chemical compound, liquid air would evaporate being unchanged in its composition.

(b) *From solution in water :* The solubility of oxygen in water is greater than that of nitrogen. When air is dissolved in water and the solution thus produced is heated to expel the dissolved air, the expelled air thus obtained is found to contain greater percentage of oxygen than oridnary air. If air were a compound, the solution of air in water would not have altered its composition.

(c) *By diffusion :* When air is passed through a porous tube, nitrogen being lighter than oxygen diffuses more quickly than oxygen. The diffused air thus obtained is found to contain greater percentage of nitrogen. If air were a chemical compound, its constituents could not be separated by this simple process.

• NITROGEN •

Symbol : N	**Atomic No. : 7**	**Atomic wt : 14·008**
Electronic configuration :	**$1s^2, 2s^2 2p^3$**	**Oxidation No. (−3), (−2), (+1), (+2), (+3), (+4), (+5)**

Nitrogen was discovered in 1772 by **Daniel Rutherford,** a sottish chemist. **Lavoisier,** proved its elementary nature and called it *'azote'* (= without life). The present name nitrogen was given by **Chaptal** as it is present in **nitre.**

Elementary nitrogen occurs in air and constitutes nearly four-fifths of its volume. In a combined state it is found in nitre (KNO_3), chile saltpetre ($NaNO_3$) and anmonium salts. Nitrogen is an essential constituents of all vegetable and animal proteins.

2.5. Comparison of nitrogen with the other members of Group VB.

Period	Gr VB
2	$_{7}N$
3	$_{15}P$
4	$_{33}As$
5	$_{51}Sb$
6	$_{83}Bi$

Nitrogen is the first element of group V B in the second period of the periodic table. Nitrogen differs from the other members of this group due to the following inherent properties—(i) the size of N-atom is the smallest, (ii) nitrogen is the strongest electronegative element in the group, (iii) there is no *'d'* orbital in N atom. The main points of differences are given below—

(1) Nitrogen is a gas at ordinary temperature while the other members of the group are solid.

(2) Nitrogen is diatomic ($N{\equiv}N$) whereas the others are tetra atomic e.g., P_4, As_4.

(3) Nitrogen does not exhibit allotropy (solid N_2 exhibits allotropy) while the other members of the group (excepting Bi) exhibit allotropy.

(4) Nitrogen occurs in free state in nature but the other members of the group do not occur in free state.

(5) Nitrogen exhibits a number of oxidation states e.g., -3 in NH_3, -2 in N_2H_4, -1 in NH_2OH, $+1$ in N_2O, $+2$ in NO, $+3$ in N_2O_3, $+4$ in NO_2 and $+5$ in N_2O_5. The other elements of this group do not exhibit such a number of oxidation states.

(6) Due to the absence of *'d'* orbital nitrogen can not expand its octet hence its valency is 3 while other members except bismuth, form *tri* and *penta* valent compounds. Bismuth is always trivalent due to **inert pair effect** [see Vol II].

(7) The hydride of nitrogen (NH_3) is stable and not poisonous, while the hydrides of other members are progressively less stable and poisonous. Due to the small size and high electro-negativity of nitrogen, NH_3 molecules get associated with each other due to the formation of hydrogen bond in between them and as a result the b.p. of NH_3 is much greater than those of the hydrides of the other members.

(8) Nitrogen trichloride is very unstable compound while the trichlorides of the other members are progressively stable. Pentachloride of nitrogen does not exist but P, As and Sb form stable pentachlorides.

(9) Nitrogen cannot form sulphide compound, where as all other members of this group do form sulphide compounds.

(10) All the elements in +3 state are good electron pair donor. Nitrogen exhibits this property to the maximum extent, but due to the absence of *'d'* orbital nitrogen can not act as electron pair acceptor. Other members having vacant *'d'* orbital in their valence shell act as electron pair acceptor.

(11) The catenation property is most pronounced in nitrogen. Straight chain compounds having 8 N-atoms are known. In the other members of this group catenation is limited to only two atoms. Four P-atoms are self linked in P_4 molecule. Bond energy shows that C−C bonds are more stable than N−N or P−P bonds.

N−N = 20 k cals/mole, P−P = 18·8 k cal/mole, C−C = 58·6 k cal/mol

(12) Inspite of being the third most electro-negative element, nitrogen is an inert element. The triple bond present in nitrogen molecule being very strong (bond length 1·09Å), it requires a high energy to split the N_2 molecule to form active nitrogen atom. Due to the presence of single bond in their molecules, the other members of the group are reactive as they require less energy to split the single bonds of their molecules.

• Nitrogen (N ≡ N), carbon monoxide (C ≡ O) and CN^- ion (− C ≡ N) are isoelectric yet the later two are very reactive—Explain why.

This is due to the fact that though they have the same distribution of electrons in the bonding orbitals, the nitrogen molecule is none polar and the N atom have high ionisation energy.

• The other members of Group V B can form tri halides as well as penta halides, but nitrogen can form only unstable tri halide but not penta halide—Explain why.

The electronic configuration of nitrogen is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. Thus it is found that there are half-filled *p*-orbitals in nitrogen atom which are able to overlap with the other half-filled *p*-orbitals of three atoms of halogen ($ns^2\ np_x^2\ np_y^2\ np_z^1$). As a result 1N-atom forms three covalent bonds (N−X) with three atoms of halogens to form NX_3 molecule. In order to form additional bonds, the N-atom should contain more half filled or vacant orbitals in its L shall. Due to the absence of 3*d* orbitals, only 3 half-filled orbitals are available in N-atom and consequently it can form tri halides and can not form penta halides. In other members of Group V B vacant *'d'* orbitals are available and so the other members except Bi, can form penta halides.

2.6. Laboratory method of preparation of nitrogen.

[A] **Principle :** Pure nitrogen is obtained in the laboratory by heating a concentrated solution of *ammonium nitrite*. But as ammonium nitrite is very unstable, its thermal decomposition may take place with explosion. With a view to avoiding this, a concentrated solution containing *sodium nitrite* and *ammonium chloride* is heated gently.

In the first step ammonium chloride reacts with sodium nitrite to form ammonium nitrite and sodium chloride. In the second step the ammonium nitrite thus produced is thermally decomposed to give nitrogen and water.

$$NaNO_2 + NH_4Cl = NH_4NO_2 + NaCl$$
$$NH_4NO_2 = N_2 + H_2O$$

[B] **Procedure :** (i) A concentrated solution containing equimolecular quantities of sodium nitrite and ammonium chloride is taken in a round bottomed flask fitted with a thistle funnel and a delivery tube. The end of the thistle funnel should always be kept under the surface of the solution in the flask (ii) The end of the delivery tube is kept under water in a pneumatic trough. (iii) The flask is clamped to a stand and kept on a wire gauze on a tripod stand. (iv) The solution in the flask is now gently heated when thermal decomposition of ammonium nitrite takes place with the evolution of nitrogen. (v) After allowing the air inside the flask to escape, a gas jar filled with water is inverted over the end of the delivery tube. (vi) Nitrogen collects in the gas jar by the displacement of water.

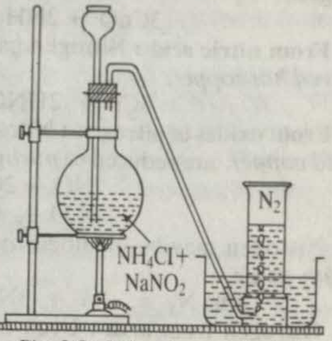


Fig. 2.5 : Laboratory method of preparation of N_2

[C] **Purification :** Nitrogen thus obtained is found to the contain a little *chlorine, ammonia, different oxides of nitrogen* and *moisture* as impurities.

(i) The gas is passed through a concentrated solution of *caustic soda* to remove *chlorine*. (ii) It is then passed through conc. H_2SO_4 to remove ammonia and moisture. (iii) Finally the gas is passed through a red hot tube containing copper turnings, when the oxides of nitrogen are reduced to nitrogen. $2NO + 2Cu = 2CuO + N_2$ Pure nitrogen thus obtained is collected over mercury.

- **Precautions :**

(i) Ammonium nitrite is very unstable compound and so the thermal decomposition of ammonium nitrite may take place with explosion. To avoid this the flask should be heated carefully and gently. (ii) Burner should be removed as soon as nitrogen begins to evolve. (iii) If the reaction proceeds vigorously the flask should be cooled.

2.7. Other methods of preparation of nitrogen.

1. **From ammonium dichromate :** Nitrogen may be obtained by heating gently the red crystals of ammonium dichromate. Violent action takes place producing flashes of light and nitrogen is liberated and a green residue of *chromic oxide* is left behind. The violent reaction may be controlled if a concentrated solution containing $K_2Cr_2O_7$ and NH_4Cl is used.

$$\begin{aligned}(NH_4)_2Cr_2O_7 &= N_2 + Cr_2O_3 + 4H_2O\\ K_2Cr_2O_7 + 2NH_4Cl &= N_2 + 2KCl + Cr_2O_3 + 4H_2O.\end{aligned}$$

2. **By the oxidation of ammonia :**

(a) Nitrogen is obtained when *ammonia is oxidised by chlorine or bromine.* In each case excess of ammonia must be used to prevent the formation of highly explosive NCl_3 or NBr_3.

$$\begin{aligned}2NH_3 + 3Cl_2 &= N_2 + 6HCl\\ 6NH_3 + 6HCl &= 6NH_4Cl\\ \hline 8NH_3 + 3Cl_2 &= 6NH_4Cl + N_2\end{aligned}$$

(b) Nitrogen is liberated when ammonia is treated with *bleaching powder.*

$$2NH_3 + 3Ca(OCl)Cl = 3CaCl_2 + N_2 + 3H_2O$$

(c) When *ammonia is passed over heated cupric oxide,* ammonia is oxidised to nitrogen.

$$3CuO + 2\overset{-3}{N}H_3 = 3Cu + \overset{0}{N}_2 + 3H_2O$$

3. **From nitric acid :** Nitrogen gas is liberated when nitric acid vapour is passed over *red hot copper.*

$$5Cu + 2HNO_3 = 5CuO + N_2 + H_2O$$

4. **From oxides of nitrogen :** Nitrous oxide, nitric oxide etc., on being passed over *heated copper,* are reduced to *nitrogen.*

$$2NO + 2Cu = 2CuO + N_2$$
$$N_2O + Cu = CuO + N_2$$

5. Nitrogen may be obtained *by the thermal decomposition of sodium azide or barium azide.*

$$2NaN_3 = 2Na + 3N_2 \qquad Ba(N_3)_2 = Ba + 3N_2$$

6. **Nitrogen from urea :** Urea on treatment with alkaline *sodium hypobromite* evolves N_2.

$$CO(NH_2)_2 + 3NaOBr = N_2 + CO_2 + 3NaBr + 2H_2O$$

7. **Nitrogen from air :** Air is chiefly a mixture of nitrogen and oxygen in the ratio 4 : 1 (approx.) by volume. Nitrogen can be obtained simply by removing oxygen from air. Removal of oxygen from air is carried out by different processes.

(a) **Removal of oxygen from air by red hot copper :**

In addition to oxygen and nitrogen, air contains a small amount of CO_2, water vapour and traces of inert gases. (i) At first air is passed through a solution of KOH when CO_2 is removed. (ii) It is then passed through conc. H_2SO_4 or P_2O_5 and thus water vapour is removed from air. (iii) The air thus freed from CO_2 and water vapour, is slowly passed through a long hard glass tube containing some copper turnings. The tube is placed horizontally in a furnace. One end of the tube is connected with an inlet tube for the entry of air and the other end is connected with a delivery tube. The free end of the delivery tube is kept under water in a pneumatic trough. The copper turnings in the tube are strongly heated and air is slowly passed over it. At high temperature, oxygen of air combines with heated copper to form cupric oxide, and the unreacted nitrogen passes out through the delivery tube and is collected in a gas jar by the displacement of water.

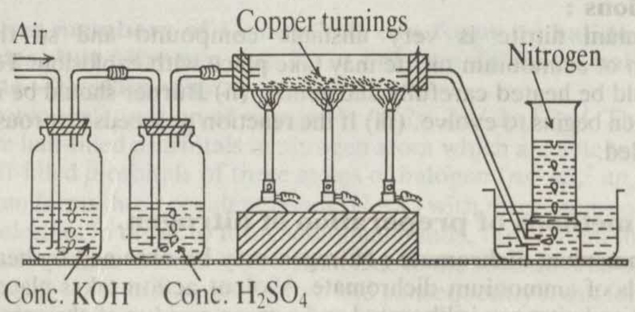


Fig. 2.6 : Preparation of Nitrogen from air

$$CO_2 + 2KOH = K_2CO_3 + H_2O \; ; \quad 2Cu + O_2 = 2CuO.$$

• **Nitrogen obtained from air is found to be slightly heavier than the nitrogen obtained from its compounds in the laboratory—Explain why :**

In addition to nitrogen and oxygen, air contains small amount of carbon di-oxide, water vapour and inert gases like helium, neon, argon, krypton, xenon etc. The oxygen, CO_2 and water vapour are removed easily from air by chemical means, but due to their chemical inertness, the inert gases do not react with any substance and consequently it is not possible to remove these inert gases from nitrogen obtained from air. Thus these inert gases remain with the nitrogen obtained from air. Excepting helium, each of the inert gases is heavier than nitrogen.

In the laboratory nitrogen is obtained by the decomposition of nitrogeneous compounds. Thus N_2 is obtained by the thermal decomposition of NH_4NO_2. The N_2 thus obtained contains impurities (Cl_2, NH_3, water vapour, oxides of N_2 etc.) which are easily removed by chemical process and pure N_2 can be obtained. That is why N_2 obtained from air is heavier than the nitrogen obtained from its compounds.

(b) **Removal of oxygen from air by burning phosphorus :**

This process has already been described previously in discussion with the composition of air. Nitrogen obtained by this process is not pure as it contains inert gases in traces. Moreover, it is not possible to remove O_2 completely from air by this process.

(c) **By fractional distillation of liquid air :**

Nitrogen required for industrial purpose is obtained by the fractional distillation of liquid air. This process has already been described previously in connection with the preparation of oxygen from air.

2.8. Properties of nitrogen.

[A] **Physical :** (i) Nitrogen is a colourless, odourless and tasteless gas. (ii) It is slightly lighter than air and almost insoluble in water. (iii) It is not poisonous but does not support respiration. (iv) It can be liquefied to a colourless liquid (b.p. −195·8°C) which freezes to a white solid (m.p. −209·8°C).

[B] **Chemical :** Two N-atoms are joined with each other by covalent bonds by sharing 3 electron pairs. This bond is very strong and as a result nitrogen is inert in nature. It contains one sigma (σ) and two pie (π) bonds. Although N_2 molecule contains two lone pairs, it has no basic property as the lone pairs occupy *sp* hybrid orbitals, hence firmly bound towards the nucleus. So they are not available for protonation.

1. Nitrogen is *incombustible* and a *non supporter of combustion.*

2. **Action on metals :** At ordinary temperature nitrogen does not react with metals, but reacts with heated metals like *calcium, magnesium, aluminium* to produce the respective *metallic nitrides.*

These metallic nitrides react with boiling water to produce *ammonia* and *metallic hydroxides.*

$$3Mg + N_2 = Mg_3N_2 \;; \qquad Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$
$$3Ca + N_2 = Ca_3N_2 \;; \qquad Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3$$
$$2Al + N_2 = 2AlN \;; \qquad AlN + 3H_2O = Al(OH)_3 + NH_3$$

3. **Action on non metals :** Nitrogen combines with many non metals at high temperature.

(i) *With hydrogen :* At above 550°C under a *pressure* of *200 atmosphere,* in presence of *iron catalyst,* nitrogen directly combines with hydrogen to produce *ammonia.*

$$N_2 + 3H_2 \xrightarrow[200\,\text{Atm}]{550^\circ\text{C}} 2NH_3 + 22{\cdot}4\,\text{k cals}$$

(ii) *With oxygen :* At 3000°C under the influence of *electric spark, nitrogen* combines with oxygen to from *nitric oxide.* The reaction is endothermic.

$$N_2 + O_2 \rightleftharpoons 2NO - 43{\cdot}2\text{k cals}$$

(iv) *With boron and silicon :* At *red hot* condition boron and silicon combine with nitrogen to yield the corresponding *nitrides.*

$$2B + N_2 = 2BN, \qquad 3Si + 2N_2 = Si_3N_4$$

4. *Action on Calcium carbide :* Heated *calcium carbide* reacts with nitrogen at 1100°C to yield *calcium cyanamide* and *carbon.* The mixture of calcium cyanamide and carbon is brown coloured and its commercial name is *nitrolim.* It is used as chemical fertiliser. Calcium cyanamide undergoes hydrolysis with superheated steam to yield *ammonia* and *calcium carbonate.*

$$CaC_2 + N_2 = CaCN_2 + C$$
$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3 \uparrow$$

- **Tests for nitrogen :**

(i) Nitrogen is a colourless and odourless gas in which a lighted taper is extinguished, but it does not turn lime water milky like CO_2.

(ii) A burning magnesium ribbon continues to burn in it producing white magnesium nitride. This white residue on treatment with boiling water gives ammonia which is recognised by its characteristic pungent smell.

$$3Mg + N_2 = Mg_3N_2 \; ; \qquad Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3 \uparrow$$

- **Uses of nitrogen :**

(i) Due to its chemical inertness it is used (a) for filling electric bulbs and in making gas thermometers, (b) in creating inert atmosphere in some chemical and metallurgical processes.

(ii) It is used in the manufacture of ammonia, nitric acid and nitrogeneous fertilizers.

(iii) Liquid nitrogen is used as refrigerant.

- **Active nitrogen :**

It was observed by Strutt that when nitrogen is subjected to the action of electric discharge at low pressure (less than 1 mm) a bright glow appears which persists for sometime even when the discharge is stopped. This indicates the slow release of energy in the process. He found that nitrogen at this stage is more active than ordinary nitrogen. It has been called *active nitrogen.*

Properties : The active nitrogen has a short life and gradually it is converted into the ordinary form. Active nitrogen exhibits some reactions which are not exhibited by ordinary N_2.

(i) *Alkali metals* easily combine with active nitrogen at ordinary temperature to form *nitrides.*

(ii) Ca, Mg, Zn, Sn, Pb etc., are converted to corresponding nitrides when reacted with active nitrogen. It combines readily with non metals like P, S, As, to produce the corresponding nitrides.

(iii) It reacts with nitric oxide to form nitrogen and O_2.

$$2NO + 2N^{\cdot} = O_2 + 2N_2$$

(iv) With acetylene it gives HCN.

$$C_2H_2 + 2N^{\cdot} = 2HCN$$

(v) It reacts with atomic hydrogen to produce ammonia.

$$3H + N^{\cdot} = NH_3$$

It has been suggested that active nitrogen is a mixture of atomic nitrogen and molecular nitrogen ($N_2 + N$). Due to the presence of nitrogen in atomic state, the atomic nitrogen is so active.

2.9. Nitrogen cycle in nature.

Nitrogen is indispensable for the growth of plants and animals. Nitrogen is an essential constituent of a class of organic compounds known as *proteins.* It is therefore extremely necessary for the living organisms. The ultimate source of nitrogen is the atmosphere, but with the exception of a few liguminous plants, neither animals nor plants are capable of assimilating nitrogen directly from atmosphere. Now let us see how nitrogen passes from atmosphere to plants and animals and is used up to produce various useful products like ammonia, nitric acid etc., and still the percentage of nitrogen in atmosphere remains constant. This is due to the fact that nitrogen from nature is continuously passing back to the atmosphere.

Definition of nitrogen cycle : *The process of conversion of atmospheric nitrogen into various types of nitrogeous compounds necessary for the life process of plants and animals, and the decomposition of these nitrogeneous compounds back to atmosphere as free nitrogen, is called 'nitrogen cycle'.*

This phenomenon takes place through the following steps—

(1) **Transfer of atmospheric nitrogen to soil :**

(a) ***By lightning discharges :***

(i) Nitrogen and oxygen of air combine to produce *nitric oxide* during lightning discharges in the upper atmosphere.

$$N_2 + O_2 \xrightarrow{\text{lightning}} 2NO$$

(ii) The nitric oxide thus produced is *further oxdised* by excess of atmospheric oxygen to *nitrogen di-oxide.*

$$2NO + O_2\,(\text{air}) = 2NO_2$$

(iii) Nitrogen dioxide reacts with rain water to form HNO_3.

$$4NO_2 + 2H_2O + O_2 = 4HNO_3.$$

(iv) The nitric acid is washed down by rain water into the soil where it is converted to soluble nitrates by reacting with bases present in the soil, which enables the soil to act as store house of plant food.

$$2HNO_3 + \underset{\text{base in the soil}}{CaCO_3} = Ca(NO_3)_2 + CO_2 + H_2O$$

(b) ***By symbiotic bacteria :*** Some liguminous plants like peas, beens, clover etc., have small nodules on their roots. These nodules are the colonies of a special type of nitrogen fixing bacteria called *symbiotic bacteria.* These bacterias have the power to convert atmospheric nitrogen directly into compounds which the plants can easily assimilate. Some *algae* and *fungi* have the power to utilise atmospheric nitrogen.

(c) ***In the form of nitrogeneous manures :*** The atmospheric nitrogen is being daily converted into manures like *ammonium sulphate, urea, calcium cyanamide* etc. *These are added to the soil and serve as reservoirs of plant food in the soil.*

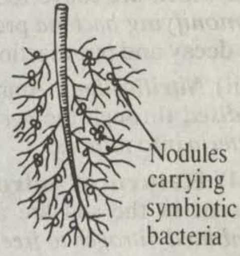


Fig 2.7

(2) **Conversion of nitrogeneous compounds in the soil into plant and animal proteins :**

Nitrogen present in the soil in the form of soluble nitrates, is absorbed by plants through their roots and are finally converted into plant proteins.

Animals are not in a position to assimilate nitrogen directly either from air or from soluble nitrates of the soil. *Herbivorous animals eat plants and thus they* get

their supply of proteins. *Carnivorous animals* get their supply of proteins from other animals which they eat.

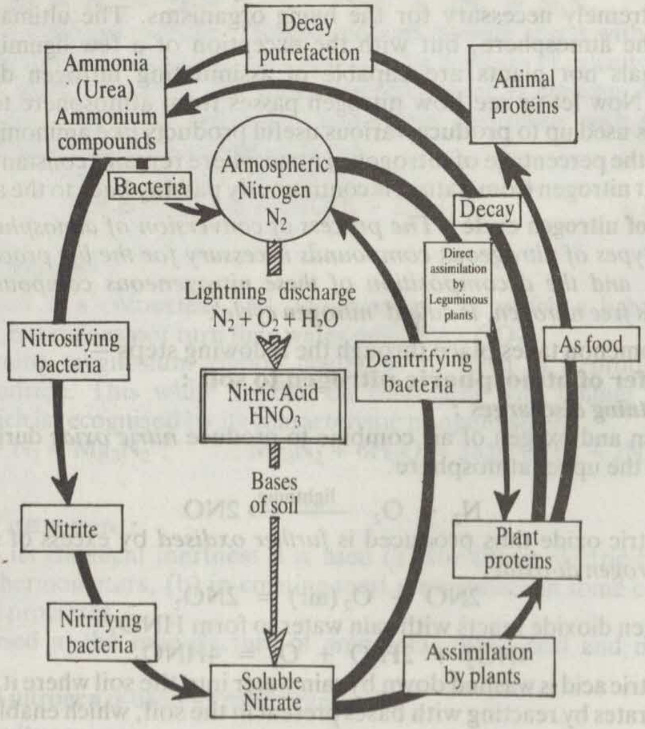


Fig 2.8 : Nitrogen cycle in nature

(3) **Return of nitrogen from plants and animals to soil :**

(i) ***Ammonification :*** The major parts of nitrogen consumed by animals is excreted as waste products and is returned to the soil in the form of *amino acids* and *urea* which are converted to *ammonia and ammonium salts* through the agency of *ammonifying bacteria* present in the soil. *Ammonia* is also liberated in the soil by the decay and putrafaction of dead animals and plants.

(ii) ***Nitrification :*** Ammonia and ammonium salts thus produced in the soil are *oxidised* through the *agency of nitrosifying bacteria* into *nitrites* and by *nitrifying bacteria* into *nitrates.*

(4) **Return of nitrogen to atmosphere :** The nitrogeneous compounds present in the soil are also acted upon by *de nitrifying bacteria* which convert *combined nitrogen to free nitrogen which* returns to atmosphere.

Thus a continuous cycle of changes known as nitrogen cycle is going on in nature.

2.10. Fixation of nitrogen.

Nitrogen present in the atmosphere is free nitrogen whereas nitrogen present in various nitrogeneous compounds is known as **fixed nitrogen.** *The conversion of free atmospheric nitrogen into useful nitrogeneous compounds is called fixation of nitrogen.*

The chief methods by which atmospheric nitrogen can be fixed as important nitrogeneous compounds are described below—

1. **Birkland and Eyde process :**

When air is passed through an electric arc producing high temperature (about 3000°C), nitrogen combines with oxygen to form nitric oxide. The nitric oxide thus obtained when cooled combines with more oxygen to give nitrogen di-oxide. Nitrogen di-oxide on being treated with water gives nitric acid.

$$N_2 + O_2 = 2NO$$
$$2NO + O_2 = 2NO_2$$
$$3NO_2 + H_2O = 2HNO_3 + NO$$

2. **Harber process :** Nitrogen is obtained from liquid air. A mixture of nitrogen and hydrogen in the ratio 1 : 3, under 200 atmosphere pressure is passed over iron powder heated to 550°C, when nitrogen directly combines with hydrogen to produce ammonia.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat}$$

Ammonia thus obtained is oxidised by air in presence of heated platinum gauze (700°C) to form nitric oxide. Nitric oxide thus obtained is further oxdised by air to give NO_2. NO_2 reacts with water to produce HNO_3.

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$
$$2NO + O_2 = 2NO_2$$
$$3NO_2 + H_2O = 2HNO_3 + NO.$$

Ammonia and nitric acid thus obtained may be converted to ammonium salts and nitrates which are used as fertilisers.

3. **Serpeck process :** In this process a mixture of coke and alumina is heated in a current of air at 1400°C, when aluminium nitride is produced. Aluminium nitride when treated with steam yields ammonia.

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO\uparrow$$
$$AlN + 3H_2O = Al(OH)_3 + NH_3$$

4. **Cyanamide process :** Nitrogen gas is passed over calcium carbide heated to 1100°C when calcium cyanamide is produced.

$$CaC_2 + N_2 = CaNCN + C$$

The mixture of calcium cyanamide and carbon is known as *nitrolim* and is used as fertilizer.

Calcium cyanamide when treated with superheated steam ammonia is evolved.

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

Hydrides of Nitrogen :

Ammonia is the most important hydride of nitrogen. In addition to this, the other hydrides are *hydrazine* $NH_2 - NH_2$ and **hydrazoic acid** HN_3

1. **Hydrazine** (H_2N-NH_2) : It is obtained by the action of *sodium hypochlorite* on large excess of NH_3 in presence of gelatine. The reaction takes place in two steps—

Ist step : $NH_3 + NaOCl = NH_2Cl + NaOH$
2nd step : $NH_2Cl + NH_3 = NH_2-NH_2 + HCl$

It is fuming, colourless, poisonous covalent liquid. It decomposes by disproportionation to N_2 and NH_3 in presence of silica.

$$3\overset{-2}{N_2}H_4 = 4\overset{-3}{N}H_3 + \overset{0}{N_2}$$

It is weak base and powerful reducing agent. It reduces Fe^{3+} to Fe^{2+} and Cu^{2+} to Cu^+

$$4\overset{+2}{Cu}O + N_2H_4 = 2\overset{+1}{C}K_2O + N_2 + 2H_2O\ ; \quad 4\overset{3+}{Fe} + N_2H_4 = 4\overset{2+}{Fe} + N_2 + 4H^+$$

2. **Hydrazoic acid (N_3H)** : It is obtained by passing N_2O over *sodamide* at 190°C.

$$N \rightleftharpoons N = O + H_2N\,Na \rightarrow N \rightleftharpoons N = N\,Na + H_2O$$
$$N_3Na + H_2SO_4 = NaHSO_4 + N_3H.$$

It is colourless, highly poisonous and dangerously explosive liquid. It is weak acid. It dissolves many metals with the formation of azides.

• AMMONIA (NH_3) •

Molecular wt. — 17	Vapour density = 8·5

In 1774 Priestly prepared this gas by heating Sal ammoniac (ammonium chloride) with lime. Berthollet in 1785 established its composition.

2.11. Preparation of ammonia.

1. Laboratory method.

[A] **Principle :** Ammonia is prepared in the laboratory *by heating ammonium chloride* with *slaked lime* or *powdered quick lime*.

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$$
$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$$

[B] **Procedure :** (i) One part by weight of ammonium chloride is intimately mixed with 3 parts by weight of dry slaked lime and the mixture is taken in a round bottomed flask fitted with a delivery tube. (ii) The flask is then clamped to a stand and placed on a wire gauze kept on a tripod stand. (iii) The end of the delivery tube is connected to the bottom of a glass tower packed with quick lime. (iv) The flask is then heated by a burner when ammonia is evolved. (v) The ammonia thus evolved is passed through the lime tower where the moisture present in the gas is absorbed by the quick lime. (vi) The dry ammonia coming out of the tower is collected in a dry gas jar by the downward displacement of air.

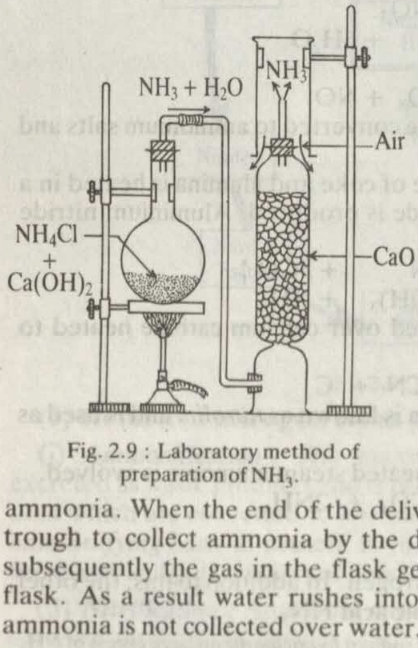


Fig. 2.9 : Laboratory method of preparation of NH_3.

• Ammonia is not collected over water—Explain why.

Ammonia is highly soluble in water. About one volume of water at ordinary temperature and pressure dissolves 1200 volumes of ammonia. When the end of the delivery tube is dipped under water in a pneumatic trough to collect ammonia by the displacement of water, the outcoming gas and subsequently the gas in the flask gets dissolved in water causing a vacuum in the flask. As a result water rushes into the hot flask causing damage. Consequently ammonia is not collected over water.

• Ammonia can not be dried by conc. H_2SO_4 or P_2O_5 or $CaCl_2$ but can be dried by quick lime—Explain why.

Ammonia is alkaline in nature and so it reacts with acid or acidic oxide with the formation of salt. Thus ammonia reacts with conc. H_2SO_4 to produce ammonium sulphate

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

Ammonia reacts with P_2O_5 (acidic oxide) producing ammonium phosphate.

$$6NH_3 + P_2O_5 + 3H_2O = 2(NH_4)_3PO_4$$

Ammonia is absorbed by calcium chloride to produce an addition compound having the composition $CaCl_2, 8NH_3$.

$$CaCl_2 + 8NH_3 = CaCl_2, 8NH_3$$

For these reasons ammonia is not dried by conc. H_2SO_4 or P_2O_5 or by anhydrous $CaCl_2$.

Ammonia is basic in nature and as quick lime is also a base, ammonia does not react with CaO and so ammonia is conveniently dried by quick lime.

- **Ammonia may also be obtained by heating ammonium salts with strong base or alkali.**

$$(NH_4)_2SO_4 + 2KOH = 2NH_3 + K_2SO_4 + 2H_2O$$
$$2NH_4NO_3 + Ca(OH)_2 = 2NH_3 + Ca(NO_3)_2 + 2H_2O$$

2. Preparation of ammonia in the laboratory at room temperature.

Ammonia gas can be obtained in the laboratory at room temperature without the application of heat.

Some solid caustic soda is taken in a dry conical flask fitted with a dropping funnel and a delivery tube. The end of the delivery tube is kept upwards. Now liquor ammonia as allowed to drop from the dropping funnel on the caustic soda. Ammonia gas is given off which comes out of the delivery tube and is collected in a dry gas jar by the down ward displacement of air.

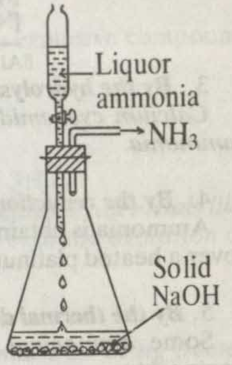


Fig. 2.10 : Preparation of NH_3 at room temperature

2.12. Other methods of preparation of ammonia.

1. ***By the hydrolysis of metallic nitrides.***

Metallic nitrides (calcium nitride, magnesium nitride, aluminium nitride) on being treated with boiling water, metallic hydroxides and ammonia are produced.

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

2. ***By the reduction of metallic nitrates or nitrites.***

Metallic nitrates or nitrites are reduced to ammonia by heating it with zinc dust or aluminium powder and concentrated sodium or potassium hydroxide solution.

$$\begin{array}{c}[2NaOH + Zn = Na_2ZnO_2 + 2H] \times 4 \\ NaNO_3 + 8H = NaOH + NH_3 + 2H_2O \\ \hline NaNO_3 + 4Zn + 7NaOH = 4Na_2ZnO_2 + NH_3 + 2H_2O\end{array}$$

[To balance the equation by ion electron method :

Half reaction for oxidation—$Zn^0 + 4OH^- - 2e = ZnO_2^{2-} + 2H_2O$ ....(1)

Half reaction for reduction $NO_3^- + 6H_2O + 8e = NH_3 + 9OH^-$ ....(2)

By adding (1) and (2) after making equal members of electrons

$$\begin{array}{c}[Zn^0 + 4OH^- - 2e = ZnO_2^{2-} + 2H_2O] \times 4 \\ NO_3^- + 6H_2O + 8e = NH_3 + 9OH^- \\ \hline 4Zn + NO_3^- + 7OH^- = NH_3 + 4ZnO_2^{2-} + 2H_2O]\end{array}$$

$$\begin{array}{c}[2NaOH + Zn = Na_2ZnO_2 + 2H] \times 3 \\ NaNO_2 + 6H = NaOH + NH_3 + H_2O \\ \hline NaNO_2 + 5NaOH + 3Zn = 3Na_2ZnO_2 + NH_3 + H_2O\end{array}$$

$$\begin{array}{c}[Al + NaOH + H_2O = NaAlO_2 + 3H] \times 8 \\ [NaNO_3 + 8H = NaOH + NH_3 + 2H_2O] \times 3 \\ \hline 8Al + 5NaOH + 3NaNO_3 + 2H_2O = 8NaAlO_2 + 3NH_3\end{array}$$

[To balance the equation $8Al + 3NaNO_3 + 5NaOH + 3H_2O = 3NH_3 + 8NaAlO_2$ **by ion electron method.**

Half reaction for oxidation. $Al + 4OH^- - 3e = AlO_2^- + 2H_2O$ ......(1)
Half reaction for reduction. $NO_3^- + 6H_2O + 8e = NH_3 + 9OH^-$ ......(2)
by adding (1) and (2) after making equal number of electrons

$$[Al + 4OH^- - 3e = AlO_2^- + 2H_2O] \times 8$$
$$[NO_3^- + 6H_2O + 8e = NH_3 + 9OH^-] \times 3$$
$$8Al + 3NO_3^- + 5OH^- + 2H_2O = 3NH_3 + 8AlO_2^-]$$

3. ***By the hydrolysis of Calcium Cyanamide :***
Calcium cyanamide on treatment with super heated steam under pressure yields ammonia.

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

4. ***By the reduction of nitric oxide or nitrogen di-oxide :***
Ammonia is obtained by passing a mixture of *nitric oxide* (or NO_2) and *hydrogen* over a heated platinum catalyst. $2NO + 5H_2 = 2NH_3 + 2H_2O$

$$2NO_2 + 7H_2 = 2NH_3 + 4H_2O$$

5. ***By the thermal decomposition of ammonium salts :***
Some *ammonium salts* are *thermally decomposed* to give ammonia at high temperature.

$$(NH_4)_2SO_4 = NH_3 + NH_4HSO_4$$
$$2(NH_4)_3PO_4 = 6NH_3 + P_2O_5 + 3H_2O$$

2.13. Properties of ammonia.

[A] **Physical** : (i) Ammonia is a colourless gas having a pungent smell. (ii) It is lighter than air. (iii) It is highly soluble in water. At ordinary temperature and pressure 1 volume of water dissolves about 1200 volumes of ammonia. (iv) Ammonia gas liquefies when cooled under pressure to a colourless liquid boiling at −33·4°C. It is converted to ice like solid at −78°C .

[B] **Chemical :**

(1) ***Basic nature :*** Ammonia exhibits all the reactions of a typical base. It turns red litmus solution blue and forms salts with acids. When comes in contact with hydrogen chloride, it gives a dense white fumes of solid ammonium chloride. *This is an example of the formation of a solid product by the interaction of two gases.*

$$NH_3(g) + HCl(g) = NH_4Cl(s)$$

Its aqueous solution is known as ammonium hydroxide which ionises as NH_4^+ and OH^- *ions.*

$$NH_3 + H_2O = NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

(2) ***Action on oxygen :*** (a) Ammonia does not support combustion but burns in an atmosphere of oxygen with a *yellow flame.* During this combustion ammonia is *oxidised* by oxygen to produce *nitrogen.*

$$4\overset{-3}{N}H_3 + 3O_2 = 2\overset{0}{N}_2 + 6H_2O$$

(b) When a mixture of ammonia and oxygen is quickly passed over heated *platinum gauze* heated to 700°C, ammonia is *oxidised catalytically to nitric oxide* [Ostwald's proces for the manufacture of nitric acid].

$$4\overset{-3}{N}H_3 + 5O_2 = 4\overset{+2}{N}O + 6H_2O + \text{Heat}$$

(3) ***Action on chlorine :*** (a) *Excess of ammonia is oxidised by chlorine to produce nitrogen* and chlorine is reduced to *hydrogen chloride.* The acid thus formed further reacts with the rest of ammonia to form ammonium chloride.

$$\begin{array}{l} 2NH_3 + 3Cl_2 = N_2 + 6HCl \\ 6NH_3 + 6HCl = 6NH_4Cl \\ \hline 8\overset{-3}{N}H_3 + 3Cl_2 = 6NH_4Cl + \overset{0}{N}_2 \end{array}$$

(b) *With excess of chlorine* ammonia is oxidised to form an explosive compound *nitrogen trichloride.*

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl$$

(c) *Bleaching powder* oxidises ammonia to *nitrogen.*

$$3Ca(OCl)\,Cl + 2\overset{-3}{N}H_3 = 3CaCl_2 + \overset{0}{N}_2 + 3H_2O$$

(4) **Action on metals :** When ammonia gas is passed over *heated alkali metals like sodium or potassium* at about 360°C , *amides* are produced with the evolution of hydrogen.

$$2NH_3 + 2Na = \underset{\text{(Sodamide)}}{2NaNH_2} + H_2$$

This reaction proves that ammonia contains hydrogen. Amides on being treated with water are decomposed to give *ammonia and hydroxides*

$$NaNH_2 + H_2O = NaOH + NH_3\uparrow$$

(5) **Reducing property of ammonia :**

At ordinary temperature ammonia does not possess reducing property but when ammonia gas is passed over red hot *cupric oxide,* the later is reduced to *metallic copper* and ammonia is oxidised to nitrogen.

$$3\overset{+2}{Cu}O + 2NH_3 = 3\overset{0}{Cu} + N_2 + 3H_2O$$

Thus *lead monoxide* is also reduced to metallic *lead* by ammonia.

$$3PbO + 2NH_3 = 3Pb + N_2 + 3H_2O$$

(6) **Action on carbon di-oxide :**

(a) *Aqueous solution of ammonia* reacts with carbon di-oxide yielding *ammonium carbonate.*

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$$

(b) At *200°C under 150 atmosphere pressure,* ammonia reacts with carbon di-oxide to produce *urea :*

$$CO_2 + 2NH_3 = CO(NH_2)_2 + H_2O$$

(7) **Action on metallic salts :**

Aqueous solution of ammonia (ammonium hydroxide) reacts with *solutions of ferric salts,* with the formation of *reddish brown precipitate of ferric hydroxide.* Ammonium hydroxide on being treated with *aqueous solutions of aluminium salts, white gelatenous precipitate of aluminium hydroxide* is obtained. The colour of the produced hydroxides helps to detect the metals.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3\downarrow + 3NH_4Cl$$
$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3\downarrow + 3(NH_4)_2SO_4$$

(8) **Formation of complex salts :**

Ammonia reacts with some metallic salts producing soluble complexes.

- **Ammonia is a good complexing agent—Explain why.**

The N-atom in NH_3 molecule has a lone pair of electrons. Due to the presence of this lone pair of electrons on N-atom, it can coordinate with other atoms or cations which need electron pair for their stability, with the formation of complex salts.

(a) *With copper salts :* When ammonium hydroxide is gradually added to *copper sulphate solution,* a *bluish white precipitate of basic copper sulphate* is first obtained which dissolves on addition of excess of ammonium hydroxide to form a *deep blue solution of* the complex *cupro ammonium sulphate or copper tetra amine sulphate.*

$$2CuSO_4 + 2NH_4OH = \underset{\text{bluish white ppt}}{CuSO_4, Cu(OH)_2\downarrow} + (NH_4)_2SO_4$$

$$CuSO_4, Cu(OH)_2 + (NH_4)_2SO_4 + 6NH_4OH = 2[Cu(NH_3)_4]SO_4 + 8H_2O$$

(b) (i) *Silver nitrate* on being treated with ammonium hydroxide at first a *white precipitate of silver hydroxide* is obtained which is quickly converted to *brown silver oxide.* On addition of excess of ammonium hydroxide, the produced silver oxide dissolves to form a clear solution of complex *argento ammonium hydroxide.*

$$AgNO_3 + NH_4OH = AgOH\downarrow + NH_4NO_3$$
$$2AgOH = Ag_2O + H_2O$$
$$Ag_2O + 4NH_4OH = 2[Ag(NH_3)_2]OH + 3H_2O$$

When excess of ammonium hydroxide is added to *silver chloride* suspended in water, it dissolves to give a clear solution of the *complex argento ammonium chloride.*

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O.$$

(c) *Aqueous solution of zinc salts* reacts with ammonium hydroxide to produce a *white precipitate* of *zinc hydroxide* which dissolves in excess of ammonium hydroxide giving a *clear solution of zinc-amino hydroxide.*

$$\begin{array}{lll} ZnSO_4 & + 2NH_4OH & = Zn(OH)_2\downarrow + (NH_4)_2SO_4 \\ Zn(OH)_2 & + 4NH_4OH & = [Zn(NH_3)_4](OH)_2 + 4H_2O \end{array}$$

(9) ***Formation of addition compounds :***

Anhydrous *calcium chloride, zinc chloride* etc., absorbs ammonia producing *addition products.*

$$CaCl_2 + 8NH_3 = CaCl_2, 8NH_3$$
$$ZnCl_2 + 8NH_3 = ZnCl_2, 8NH_3$$

(10) ***Action on Nessler's reagent :***

Ammonia when comes in contact with Nessler's reagent gives a brown precipitate.

$$NH_3 + 2K_2HgI_4 + 3KOH = \underset{\text{(brown ppt)}}{I[Hg - O - HgNH_2]} + 7KI + 2H_2O$$

- Aqueous solution of ammonia on being treated with potassium permanganate gives off ammonia. In neutral solution $[2KMnO_4 = 2MnO_2 + K_2O + 3O] \times 2$

$$\begin{array}{lll} 4NH_3 & + 6O & = 6H_2O + 2N_2 \\ 2K_2O & + 2H_2O & = 4KOH \\ \hline \multicolumn{3}{l}{4KMnO_4 + 4NH_3 = 4KOH + 2N_2 + 4MnO_2 + 4H_2O} \end{array}$$

- **Tests for ammonia :**

(i) It has a characteristic pungent smell.

(ii) When a drop of concentrated hydrochloric acid is added to ammonia gas, a dense-white fumes of ammonium chloride is produced.

$$NH_3 + HCl = NH_4Cl$$

(iii) Ammonia when comes in contact with Nessler's reagent, gives a brown precipitate.

- **Nessler's reagent :**

(i) *Potassium iodide solution* when added to an aqueous solution of *mercuric chloride,* a red precipitate of *mercuric iodide* is first obtained. On addition of excess KI solution this red precipitate dissolves to produce a *complex potassium mercuro* *iodide*. When excess of KOH is added to this complex, Nessler's reagent is produced.

$$\begin{array}{l} HgCl_2 + 2KI = 2KCl + HgI_2 \downarrow \\ HgI_2 + 2KI = K_2[HgI_4] \\ \hline HgCl_2 + 4KI = 2KCl + K_2[HgI_4] \end{array}$$

$$\text{Nessler's reagent} = K_2[HgI_4] + KOH.$$

(ii) Nessler's reagent is best obtained by adding excess KI solution to an aqueous suspension of mercuric oxide. The resulting solution is alkaline

$$\begin{array}{l} HgO + H_2O + 2KI = HgI_2 + 2KOH \\ HgI_2 + 2KI = K_2[HgI_4] \\ \hline HgO + H_2O + 4KI = K_2[HgI_4] + 2KOH \end{array}$$

2.14. Uses of ammonia.

(i) Ammonia is extensively used in the manufacture of *sodium carbonate* by Solvey's process and *nitric acid* by Ostwald's process.

(ii) Ammonia finds extensive use in the large scale production of different kinds of fertillizers such as *ammonium sulphate, ammonium phosphate, urea* etc.

(iii) Liquid ammonia is used as refrigerating agent in the manufacture of ice and for cold storage because of its high latent heat of vaporisation.

(iv) It is used as cleansing agent for removing grease.

(v) In the laboratory ammonia is used as an essential reagent.

2.15. Experiments to illustrate some important properties of ammonia.

(i) **Ammonia is hightly soluble in water and its aqueous solution is alkaline in nature**—*Fountains experiment*.

A dry round bottomed flask is completely filled with dry ammonia and closed with a rubber cork. Through the rubber cork passes a long narrow glass tube ending in a jet inside the flask. The flask with the narrow tube is clamped in an inverted position, the other end of the tube being dipped in water in a flask. The water of this flask is coloured with red litmus. Now the upper flask is cooled with ice cold water, when ammonia gas inside the flask contracts producing a partial vacuum inside it. As a result the red coloured water from the lower flask is pushed up by the atmospheric pressure and enters the upper flask. As soon as a little water enters the flask, the ammonia gas inside the flask dissolves in it and thus a low pressure is created in the flask. As a result water from the lower flask rushes up the jet in the form of a fountain and is turned blue. Thus, it is proved that ammonia is highly soluble in water and its aqueous solution is alkaline.

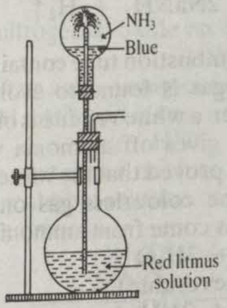


Fig. 2.11 : Fountain's experiment

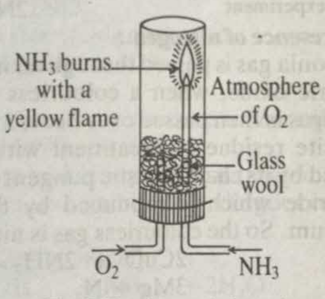


Fig. 2.12 : Ammonia burns in an atmosphere of O_2

(ii) Ammonia is not combustible but burns in an atmosphere of oxygen.

A wide tube is fitted with a rubber cork at its bottom. Through the cork pass two glass tubes. One of the glass tubes is long and the other is short which reaches just over the cork. Some glass wool is placed inside the wide tube covering the end of the short tube. Now oxygen gas is passed through the short tube. When whole of the wide tube is filled with oxygen, dry ammonia gas is passed through the long narrow tube and is ignited. It is observed that ammonia gas burns with a yellow flame in the atmosphere of oxygen [Fig. 2.12]. During its combustion NH_3 is oxidised to nitrogen.

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

(iii) Ammonia is oxidised by oxygen catalytically to produce nitric oxide.

Kraut's experiment : Liquor ammonia is warmed in a wide mouthed flask and a slow current of O_2 is passed through it. A red hot platinum spiral is lowered into the flask. As the combination of oxygen and ammonia occurs with the evolution of heat, mild explosions are heard and the platinum spiral begins to glow. Brown fumes of nitrogen dioxide are found to be formed inside the flask after some time. Ammonia is first catalytically oxidised by oxygen to form colourless nitric oxide which is further oxidised by O_2 to give brown fumes of NO_2

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

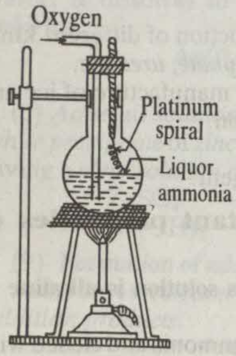


Fig. 2.13 : Kraut's experiment

- **Prove that ammonia contains nitrogen and hydrogen.**

(i) ***Presence of hydrogen :*** Ammonia is passed over metallic sodium heated to a temperature of 360°C when a colourless and odourless gas is found to evolve. The gas is collected and a burning taper is introduced in the gas when the taper is extinguished but the gas burns itself with a blue flame. Thus it is proved that the gas is hydrogen and this hydrogen has come from ammonia.

$$2Na + 2NH_3 = 2NaNH_2 + H_2\uparrow$$

(ii) ***Presence of nitrogen :***

Ammonia gas is passed through an inlet tube of a combustion tube containing red hot cupric oxide, when a colourless and odourless gas is found to evolve. The evolved gas is then passed over heated magnesium when a white residue is obtained. This white residue on treatment with boiling water gives off ammonia which is identified by its characteristic pungent smell. Thus it is proved that the white residue is a nitride which is produced by the action of the colourless gas on heated magnesium. So the colourless gas is nitrogen which has come from ammonia.

$$\begin{aligned} 2CuO + 2NH_3 &= 3Cu + N_2 + 3H_2O \\ 3Mg + N_2 &= Mg_3N_2 \text{ (white residue)} \\ Mg_3N_2 + 6H_2O &= 3Mg(OH)_3 + 2NH_3\uparrow \end{aligned}$$

- **To prove the reducing property of ammonia.**

Some black cupric oxide is taken in a combustion tube and strongly heated. Ammonia gas is passed over the heated cupric oxide through an inlet tube. After the completion of the reaction a red residue is found to be left in the combustion tube. The residue is treated with conc. HNO_3 when a blue solution is obtained with the evolution of a brown gas. Now excess of ammonium hydroxide is added to this solution when a deep blue solution of cupro ammonium salt is obtained. Thus it is proved that the red residue is nothing but metallic copper and this copper is produced by the reduction of black cupric oxide. This reduction of CuO is brought out by NH_3.

$$3CuO + 2NH_3 = 3Cu + N_2 + 3H_2O$$

- **Conversion of nitrogen to ammonia and vice versa :**

(i) ***Nitrogen → ammonia.***

Nitrogen gas is passed over strongly heated magnesium when magnesium nitride is produced as white residue. Magnesium nitride thus obtained is treated with boiling water when ammonia is given off.

$$3Mg + N_2 = Mg_3N_2$$
$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Thus, nitrogen is converted to ammonia.

(ii) ***Ammonia → nitrogen.***

Ammonia gas is passed over strongly heated cupric oxide when CuO is reduced to give metallic copper and ammonia is oxidised to nitrogen.

$$3CuO + 2NH_3 = 3Cu + N_2\uparrow + 3H_2O$$

- **Conversion of ammonia into urea :**

Liquid ammonia is made to react with liquid carbon di-oxide at 200°C under 150 atmosphere pressure in presence of a trace of moisture in an autoclave, when urea is obtained. The reaction takes place in two steps—In the first step ammonia reacts with CO_2 to form *ammonium carbamate.*

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4$$

In the second step the produced carbamate is decomposed to produce urea.

$$NH_2COONH_4 = NH_2 - CO - NH_2 + H_2O$$

- **Conversion of ammonia to nitric acid and vice versa :**

(i) ***Ammonia → nitric acid.***

A mixture of ammonia and oxygen is quickly passed over platinum gauze heated to 700°C, when ammonia is oxidised to *nitric oxide.*

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

The nitric oxide thus produced is further oxidised by oxygen to yield *nitrogen di-oxide.*

$$2NO + O_2 = 2NO_2$$

This nitrogen di-oxide on treatment with water yields nitric acid.

$$3NO_2 + H_2O = 2HNO_3 + NO$$

(ii) ***Nitric acid → ammonia.***

At first nitric acid is treated with sodium hydroxide to produce sodium nitrate.

$$HNO_3 + NaOH = NaNO_3 + H_2O$$

In the next step a mixture of sodium nitrate and zinc powder is treated with hot and concentrated solution of caustic soda when sodium nitrate undergoes reduction to yield ammonia.

$$\begin{array}{llllll} [2NaOH & + Zn & = & Na_2ZnO_2 & + 2H] & + 4 \\ NaNO_3 & + 8H & = & NaOH & + NH_3 & + 2H_2O \\ \hline \end{array}$$
$$NaNO_3 + 4Zn + 7NaOH = 4Na_2ZnO_2 + NH_3\uparrow + 2H_2O$$

- **Conversion of ammonia to ammonium sulphate and vice versa :**

(i) **Ammonia → ammonium sulphate.**

When *ammonia* and *carbon di-oxide* are passed through finely powdered *gypsum* suspended in water, *ammonium sulphate* and *calcium carbonate* are produced. Insoluble calcium carbonate is separated from the solution by filtration and the filtrate thus obtained is an aqueous solution of ammonium sulphate. This solution on evaporation and subsequent cooling yields crystals of ammonium sulphate. By this process ammonium sulphate is produced from NH_3 without H_2SO_4.

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = CaCO_3\downarrow + (NH_4)_2SO_4$$

(ii) **Ammonium sulphate → ammonia.**

Ammonium sulphate on being heated with strong alkali or base like NaOH, yields ammonia.

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O$$

2.16. Large scale preparation of ammonia—Haber's process.

Ammonia is produced in large scale by the direct combination of nitrogen and hydrogen by *Haber's process*.

[A] **Principle :** The large scale preparation of ammmonia is carried out by the direct union of nitrogen and hydrogen at high pressure (200 Atm) and at a particular temperature (550°C) in presence of a catalyst.

The synthesis of ammonia by Haber's process is worked out by the following reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22{\cdot}4 \text{ k cal}$$

[B] **Physico chemical conditions of the process to have a satisfactory yield :**

It appears from the above equation that the reaction is (a) reversible, (b) the forward reaction is exothermic, and (c) the formation of ammonia from its elements is accompanied by a *decrease in volume or in the number of molecules* [See chemical equilibrium—Vol I].

(i) ***Effect of temperature :*** As the forward reaction is exothermic the reverse reaction must be endothermic.

(a) Now according to Le Chatelier's principle, if the reaction is carried out at high temperature, the reaction will proceed in a direction where the excess heat is absorbed. As the backward reaction is endothermic, the high temperature will favour the backward reaction. As a result the yield of ammonia will be poor.

(b) If the reaction is carried out at low temperature the reaction will proceed in a direction where the loss of heat is recovered. As the forward reaction is exothermic, the lowering of temperature will favour the forward reaction with a result of better yield. Now the lowering of temperature increases the yield no doubt, but it decreases the rate of reaction to a great extent. Consequently the reversible reaction requires a longer period to attain the equilibrium. So it takes much time to get an appreciable quantity of ammonia, but so much time can not be allowed in a commercial process. So it is necessary to select a temperature at which the reaction proceeds at a satisfactory speed giving fairly good yield of ammonia. It has been found that if the reaction is carried out at 550°C the reaction proceeds at a satisfactory speed giving an appreciable yield of ammonia. Thus the reaction is carried out at 550°C and this temperature is called the *optimum temperature*.

(ii) **The influence of pressure :** As the forward reaction is accompained with a decrease in volume, according to Le Chatelier's principle high pressure will favour the forward reaction and as a result the yield of ammonia will increase. In practice, however, a pressure of 200 atmospheres is applied in the process.

(iii) **Influence of catalyst :** With a view to increasing the rate of reaction and to reach the equilibrium quickly, reduced *iron powder is used as catalyst* and *molybdenum is used as promoter*. At present *ferric oxide* is used as catalyst along with K_2O and Al_2O_3 as promoters.

(iv) **Influence of concentration :** To make the reaction proceed in the forward direction it is necessary to decrease the concentration of ammonia and this is carried out by removing the produced ammonia, quickly from the reaction chamber.

(v) A mixture of pure and dry nitrogen and hydrogen in the ratio 1 : 3 by volume is taken.

(vi) As the catalyst is very susceptible to poisoning, the gas mixture used in the process must be freed from impurities like *phosphorus, sulphur, arsenic, dust particles* etc.

[C] **Procedure :**

(i) **Preparation of the raw materials :** Pure and dry nitrogen and hydrogen are used as raw materials in Haber's process. The nitrogen used in this process is obtained by the fractional distillation of liquid air. Hydrogen is obtained by the electrolysis of water, in those places where electricity is cheap and readily available. In India electricity is not cheap and so the required nitrogen is usually obtained from the producer gas and hydrogen is obtained from water gas.

Producer gas is a mixture of carbon monoxide and nitrogen in the ratio 2 : 1 by volume. It is obtained by passing air through a bed of white hot coke.

$$2C + \underset{\text{(air)}}{(N_2 + O_2)} = \underset{\text{Producer gas}}{[2CO + N_2]}$$

Water gas is a mixture of carbon monoxide and H_2 which is obtained by passing steam over white hot coke.

$$C + H_2O = \underset{\text{Water gas}}{[CO + H_2]}$$

A mixture of N_2 and H_2 required for the synthesis of ammonia is obtained from a mixture of producer gas and water gas produced by passing air and steam alternatively over white hot coke. The timing of the two operations is adjusted in such a way so that the proportions of N_2 and H_2 in the final gas mixture may be in the ratio 1 : 3 by volume, after the removal of carbon monoxide.

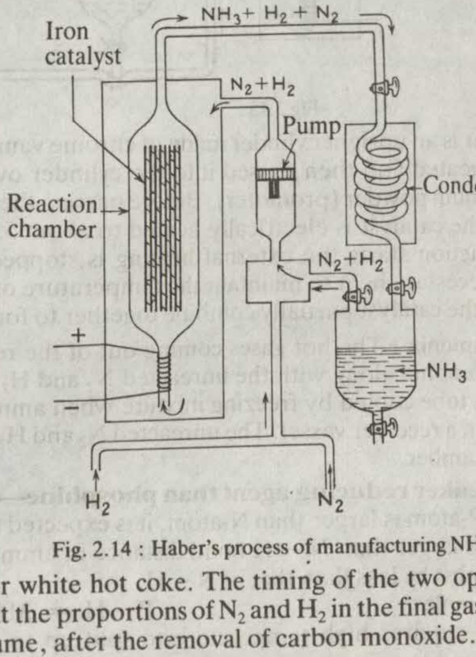


Fig. 2.14 : Haber's process of manufacturing NH_3

To remove carbon monoxide, the mixture of producer gas and water gas is mixed with calculated amount of steam and passed over *heated ferric oxide and chromic oxide at 450°C* when CO is oxidised to CO_2. The CO_2 thus produced is removed by absorbing it in water by applying *high pressure*. The last traces of carbon monoxide are removed by passing the gas mixture through *cuprous formate solution*.

$$CO + H_2O = CO_2 + H_2$$

The final gas mixture consisting of N_2 and H_2 thus obtained is dried before use.

(ii) **Synthesis of ammonia :** A mixture of nitrogen and hydrogen in the ratio 1 : 3 by volume is compressed to 200 atmospheres by a pump and is led into the reaction chamber.

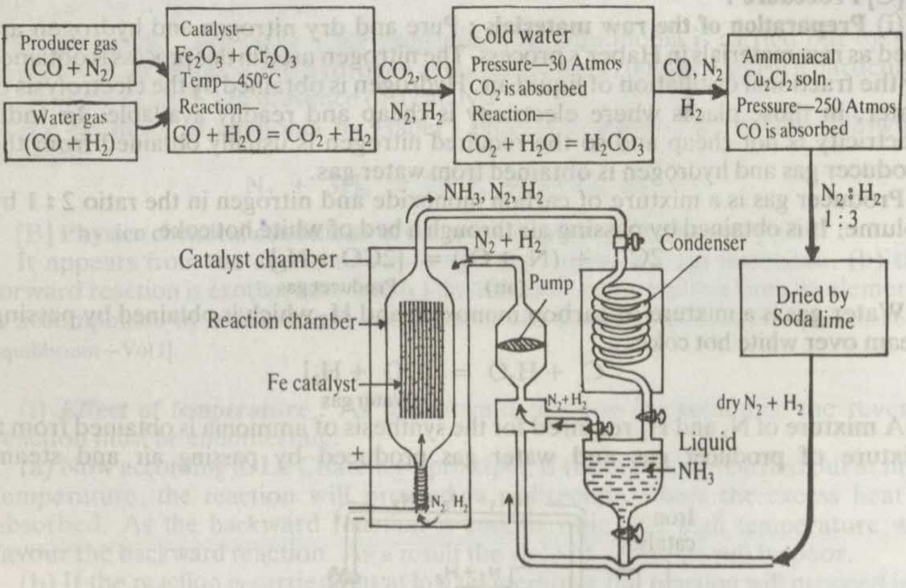


Fig 2.15 :

The reaction chamber is an upright cylinder made of chrome vanadium steel. The reacting gases are preheated and then passed into the cylinder over reduced iron (catalyst) and molybdenum powder (promoter). Before passing the gas mixture into the reaction chamber the catalyst is electrically heated to about 550°C to start the reaction. Once the reaction starts the external heating is stopped as the heat of reaction supplies the necessary heat to maintain the temperature of the catalyst. N_2 and H_2 in contact with the catalyst partially combine together to form ammonia.

(iii) **Collection of ammonia :** The hot gases coming out of the reaction chamber contains about 12% ammonia along with the unreacted N_2 and H_2. This mixture is passed through a spiral tube cooled by freezing mixture when ammonia condenses to a liquid and collects in a receiver vessel. The unreacted N_2 and H_2 are recirculated through the reaction chamber.

- **Ammonia is a weaker reducing agent than phosphine—Explain why.**

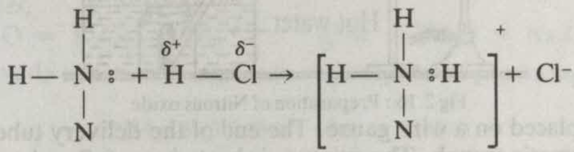
Since the size of the P-atom is larger than N-atom, it is expected that P − H bond distance in phosphine is larger than N − H bond distance in ammonia. Hence the bond energy of P − H must be less than that of N − H.

$N - H = 389 \text{ k J mole}^{-1}$ $P - H = 318 \text{ k J mole}^{-1}$

Hence N − H bond requires high temperature to split up to give off nascent hydrogen. But P − H bond requires less heat energy to break up and as a result the nascent hydrogen is easily given off from phosphine. Thus, we see that CuO is reduced by NH_3 at 350°C but $CuSO_4$ is reduced by PH_3 at room temperature. Thus it may be logically concluded that NH_3 is a weaker reducing agent than PH_3.

- **Ammonia is alkaline is nature—explain why.**

According to the electronic theory of Lewis, a base is a substance that is capable of donating a lone pair or unshared pair of electrons to proton. In ammonia molecule three H-atoms are joined to a N-atom by covalent bond. So the N-atom in ammonia molecule has an unshared pair of electrons with opposite spin. As nitrogen is a strong electronegative element, the electron pairs used in the formation of covalent bonds with hydrogen atoms, are attracted towards the nucleus of N-atom and thus the density of electrons around the N-atom is increased. As a result the lone pair of electrons suffers a force of repulsion and thus it is more easily available for protonation. This explains why ammonia exhibits alkaline property. Thus ammonia donates its lone pair of electrons to proton (H^+) of HCl and is converted to NH_4^+ ion which combines with Cl^- ions producing NH_4Cl.



$$H-\overset{H}{\underset{N}{N}}: + \overset{\delta^+}{H}-\overset{\delta^-}{Cl} \rightarrow \left[H-\overset{H}{\underset{N}{N}}:H\right]^+ + Cl^-$$

• OXIDES OF NITROGEN •

There are 5 oxides of nitrogen. In these oxides nitrogen exhibits different oxidation states.

Name of oxide	Formula	Oxidation No.
1. Nitrous oxide	N_2O	+1
2. Nitric oxide	NO	+2
3. Nitrogen trioxide	N_2O_3	+3
4. Nitrogen di-oxide	N_2O_4	+4
5. Nitrogen pentoxide	N_2O_5	+5

2.17. Nitrous oxide or Laughing gas (N_2O).

In 1772 Priestly discovered nitrous oxide. In 1779 Davy studied its physiological action and assigned a formula to it.

- **Preparation of nitrous oxide.**

Laboratory method.

[A] **Principle :** Nitrous oxide is conveniently prepared in the laboratory by *heating ammonium nitrate.* As the reaction is exothermic, ammonium nitrate begins to decompose below 200°C to give nitrous oxide, but at 250°C the reaction becomes so vigorous that explosion may take place. So it is better to heat a mixture of *ammonium sulphate and sodium nitrate.* Ammonium nitrate is produced by the reaction of the two salts which then decomposes to give off nitrous oxide.

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3$$

$$NH_4NO_3 = N_2O + 2H_2O$$

[B] **Procedure :** A mixture of ammonium sulphate and sodium nitrate is taken in a round bottomed flask fitted with a cork and a delivery tube. The flask is clamped to a stand and placed on a wire gauze. The end of the delivery tube is kept is hot water in a pneumatic trough. The mixture is heated carefully when nitrous oxide evolves which comes out through the delivery tube.

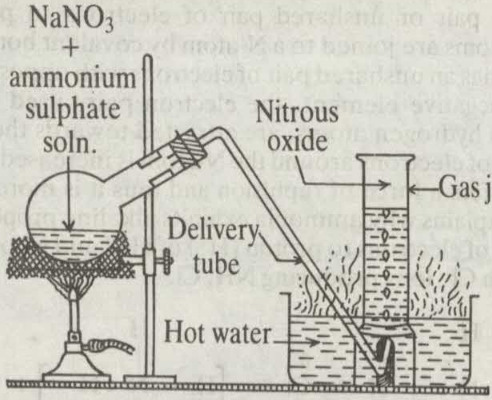


Fig 2.16 : Preparation of Nitrous oxide

[C] **Collection :** As nitrous oxide is soluble in cold water, it is collected by the displacement of hot water.

[D] **Purification :** Nitrous oxide thus obtained is contaminated with *nitric oxide, nitrogen di-oxide, ammonia, nitrogen and moisture*. The gas is purified by passing it successively through (i) *caustic soda* solution to remove NO_2, (ii) *ferrous sulphate* solution to remove NO, (iii) *conc.* H_2SO_4 to remove ammonia and moisture. The pure and dry nitrous oxide is collected over mercury.

• Other methods of preparation of nitrous oxide.

(1) ***By the action of dilute HNO_3 on Cu or Zn.***

Nitrous oxide may be obtained by the action of cold and dilute nitric acid on copper or zinc.

$$4\,Cu + 10\,HNO_3 = 4Cu(NO_3)_2 + N_2O + 5H_2O$$

(2) ***By the reduction of nitric acid.***

Nitric acid on reduction by *stannous chloride acidified with hydrochloric acid* yields nitrous oxide.

$$4SnCl_2 + 2HNO_3 + 8HCl = 4SnCl_4 + N_2O + 5H_2O$$

(3) Nitrous oxide may be obtained by *the reduction* of *nitric oxide by sulphur di-oxide.*

$$2\overset{+2}{N}O + SO_2 + H_2O = \overset{+1}{N_2}O + H_2SO_4$$

• Properties of nitrous oxide.

[A] **Physical :** (i) Nitrous oxide is a colourless gas having a faint sweet smell. (ii) It is about $1\frac{1}{2}$ times heavier than air. (iii) It is fairly soluble in cold water and more in alcohol. (iv) If inhaled it produces a kind of excitement accompanied by laughter and hence the gas is called '*laughing gas*'.

[B] **Chemical :**

(1) ***Neutral oxide :*** Nitrous oxide is a neutral oxide and so it does not change the colour of litmus.

(2) ***Decomposition :*** At ordinary temperature nitrous oxide is stable but it begins to decompose to give N_2 and O_2 at 500°C and the decomposition completes at 900°C.

(3) ***Combustibility :*** Nitrous oxide is not combustible, but a strong supporter of combustion. A glowing chip of wood burns brilliantly in this gas. Due to thermal decomposition N_2O splits up to give off nascent oxygen which supports the combustion.

(i) Pieces of burning *charcoal, sulphur, phosphorus,* continue to burn more vigorously in nitrous oxide with the formation of *nitrogen* and *the oxides* of the corresponding non-metals.

$$C + 2N_2O = CO_2 + 2N_2, \qquad S + 2N_2O = SO_2 + 2N_2$$
$$4P + 10N_2O = 2P_2O_5 + 10N_2$$

(ii) Heated *iron, copper* burn in this gas to form their corresponding oxides and N_2 is given off. Thus the metals are oxidised to form the corresponding oxides.

$$Fe + N_2O = FeO + N_2, \qquad Cu + N_2O = CuO + N_2$$

(iii) Heated *sodium* or *potassium* burns in this gas brightly producing nitrogen and *metallic peroxides.*

$$2K + 2N_2O = K_2O_2 + 2N_2 \qquad 2Na + 2N_2O = Na_2O_2 + 2N_2$$

(4) Nitrous oxide reacts wth *ammonia* with explosion producing *nitrogen* and *water.*

$$2NH_3 + 3N_2O = 4N_2 + 3H_2O$$

- **Tests for nitrous oxide :**

(i) Nitrous oxide rekindles a glowing chip of wood but does not produce brown fumes when comes in contact with nitric oxide.

(ii) *It is absorbed in alcohol* but not in alkaline pyrogallate solution.

- **Uses of nitrous oxide :**

It is used as a mild anaesthetic in dental and other minor surgical operations.

- **Structure :**

Nitrous oxide molecule is a linear molecule and is considered as renonance hybrid of the following two structures. The N−N and N−O bond lengths are 1·12 Å and 1·19 Å respectively. It is iso electronic with CO_2. It has small dipole moment.

$$:\overset{\bullet\bullet\,-}{N} = \overset{+}{N} = \underset{\bullet\bullet}{\overset{\bullet\bullet}{O}} \leftrightarrow :N\equiv\overset{+}{N} - \underset{\bullet\bullet}{\overset{\bullet\bullet\,-}{O}}:$$

- **Comparison of nitrous oxide and oxygen.**

Nitrous oxide (N_2O).	Oxygen (O_2).
(i) Colourless gas having a faint sweet smell.	(i) Colourless and odourless gas.
(ii) It is a supporter of combustion.	(ii) Oxygen is a supporter of combustion.
(iii) Does not react with colourless nitric oxide to produce brown fumes of NO_2.	(iii) Produces brown fumes of NO_2 when comes in contact with nitric oxide. $2NO + O_2 = 2NO_2$
(iv) It is absorbed in alcohol but not in alkaline pyrogallate solution.	(iv) It is absorbed in alkaline pyrogallate solution but not in alcohol.
(v) It is a neutral oxide, does not change the colour of litmus.	(v) It is a gaseous element.
(vi) Nitrous oxide causes hysteric laughter when inhaled. Inhalation of the gas for a long period causes anaesthesia.	(vi) Oxygen is a supporter of respiration.
(vii) Ammonical Cu_2Cl_2 solution has no action on N_2O.	(vii) Oxygen is absorbed by ammonical cuprous chloride solution turning the colour of the solution blue.

- **A glowing chip of wood burns more brilliantly in nitrous oxide than in oxygen—Explain why.**

When nitric oxide is subjected to heat, it decomposes at lower temperature (500°C) to produce nitrogen and nascent oxygen. $N_2O = N_2 + O\uparrow$. This nascent oxygen given off by N_2O supports the combustion. But molecular oxygen splits up to give off nascent oxygen at higher temperature. An element is more active in nascent state than in molecular state. So the combustion of glowing chip of wood takes place more vigorously in nitrous oxide than in oxygen.

2.18. Nitric oxide (NO).

Mayow prepared nitric oxide by the action of nitric acid on iron, but Priestly is regarded as the discoverer of this gas as he established this gas to be a new compound.

• Preparation of nitric oxide :

1. Laboratory method :

[A] **Principle :** Nitric oxide is prepared by the action of *moderately strong (1 : 1) nitric acid on copper turnings* at ordinary temperature.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

[B] **Procedure :** Copper turnings are placed in a Woulfe's bottle fitted with a thistle funnel and a delivery tube. Moderately strong nitric acid (1 vol acid + 1 vol water) is poured down through the thistle funnel. The end of the thistle funnel and copper turnings should remain under the surface of the acid. As soon as metallic copper comes in contact with the acid, nitric oxide begins to evolve which reacts with the air inside the Woulfe's bottle to produce reddish brown fumes of nitrogen di-oxide. The gas is allowed to escape till the brown fumes are completely expelled. The colourless gas is then collected in a gas jar by the displacement of water.

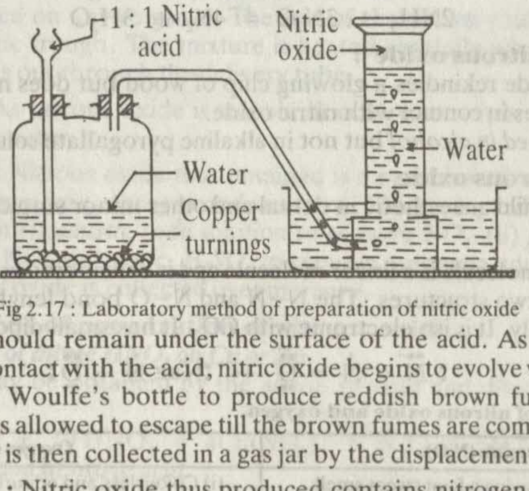


Fig 2.17 : Laboratory method of preparation of nitric oxide

[C] **Purification :** Nitric oxide thus produced contains nitrogen and other oxides of nitrogen. The gas is passed through a cold and *freshly prepared ferrous sulphate solution* when nitric oxide is absorbed yielding a dark brown solution of nitroso-ferrous sulphate. This dark brown solution on heating gives off pure nitric oxide.

2. By the reduction of potassium nitrate by acidified $FeSO_4$ solution.

A pure sample of nitric oxide can be obtained by the reduction of *potassium nitrate* by heating it with *ferrous sulphate acidified with sulphuric acid.*

$$\begin{aligned} 2KNO_3 + H_2SO_4 &= K_2SO_4 + 2HNO_3 \\ 2HNO_3 &= H_2O + 2NO + 3O \\ [2FeSO_4 + H_2SO_4 + O &= Fe_2(SO_4)_3 + H_2O] \times 3 \end{aligned}$$

$$2K\overset{+5}{N}O_3 + 4H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + 2\overset{+2}{N}O + 4H_2O$$

3. By the catalytic oxidation of ammonia :

Nitric oxide is obtained by passing a mixture of ammonia (1 vol) and air (8 vols) over platinum gauze at 700°C.

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

- **Properties of nitric oxide :**

[A] **Physical :** (i) Nitric oxide is a colourless gas slightly heavier than air. (ii) It is almost insoluble in water.

[B] **Chemical :**

(1) Nitric oxide is a *neutral oxide.* It can not change the colour of litmus solution.

(2) **Decomposition :** It is one of the most stable oxide of nitrogen. It decomposes at about 1000°C producing nitrogen and oxygen.

$$2NO \xrightarrow{1000^\circ C} N_2 + O_2$$

(3) **Supporter of combustion :** Due to its decomposition at high temperature, vigorously burning *phosphorus, sulphur, magnesium, carbon* continue to burn in nitric oxide producing their corresponding oxides. The oxygen liberated during the decomposition of nitric oxide at high temperature helps the combustion of those burning elements.

$$4P + 10NO = 2P_2O_5 + 5N_2, \qquad C + 2NO = CO_2 + N_2$$
$$2Mg + 2NO = 2MgO + N_2, \qquad S + 2NO = SO_2 + N_2$$

(4) **Oxidising property :** Nitric oxide acts as an oxidising agent, itself being reduced to nitrogen or ammonia or nitrous oxide.

(i) *A mixture of nitric oxide and hydrogen* on being passed over heated platinum black, nitric oxide is reduced to ammonia and H_2 is oxidised to H_2O.

$$2\overset{+2}{N}O + 5\overset{0}{H}_2 = 2\overset{-3}{N}H_3 + 2\overset{+1}{H}_2O$$

(ii) When nitric oxide is passed over heated *sodium, potassium, copper, iron* etc., the metals are oxidised to the corresponding oxides.

$$2\overset{0}{Cu} + 2NO = 2\overset{+2}{Cu}O + N_2, \qquad 4\overset{0}{Na} + 2NO = 2\overset{+1}{Na}_2O + N_2$$

(iii) A mixture of *carbon di-sulphide vapour* and nitric oxide burns with a blue flame and CS_2 is oxidised to *carbon monoxide.*

$$2CS_2 + 10NO = 2CO + 4SO_2 + 5N_2$$

(iv) Nitric oxide oxidises sulphurous acid to sulphuric acid.

$$2NO + H_2\overset{+4}{S}O_3 = H_2\overset{+6}{S}O_4 + N_2O$$

(5) **Reducing property :**

(i) Nitric oxide reduces *acidified solution of potassium permanganate* to a colourless solution of *manganous salt.*

$$3K\overset{+7}{Mn}O_4 + 6H_2SO_4 + 5\overset{+2}{N}O = 3KHSO_4 + 3\overset{+2}{Mn}SO_4 + 5H\overset{+5}{N}O_3 + 2H_2O$$

(ii) *Iodine* is reduced to *hydroiodic acid* by nitric oxide

$$3\overset{0}{I}_2 + 2\overset{+2}{N}O + 4H_2O = 2H\overset{+5}{N}O_3 + 6H\overset{-1}{I}$$

(6) **Formation of addition compounds :**

(i) Nitric oxide *is absorbed by* cold and *freshly prepared ferrous sulphate solution* with the formation of dark brown *nitroso ferrous sulphate.*

$$FeSO_4 + NO = Fe(NO)SO_4$$

(ii) *Nitric oxide combines with chlorine* in presence of charcoal (catalyst) to yield *nitrosyl chloride.*

$$2NO + Cl_2 = 2NOCl.$$

- **Tests for nitric oxide :**

(i) Nitric oxides produces brown fumes of nitrogen di-oxide as soon as it comes in contact with oxygen,

$$2NO + O_2 = 2NO_2$$

(ii) *It is absorbed in cold ferrous sulphate solution* producing dark brown solution of *nitroso ferrous sulphate.*

$$FeSO_4 + NO = Fe(NO)SO_4$$

- **Uses of nitric oxide :**

(i) It is extensively used in the manufacture of nitric acid. (ii) It is used to distinguish oxygen from nitrous oxide.

(ii) It is also used as an oxygen carrier in the manufacture of sulphuric acid.

- **Structure :** The NO molecule has 11 valance electrons, 5 electrons due to N atom and 6 electrons due to O atom. It is not possible for all of them to be paired and consequently NO molecule contains an odd electron. The presence of this odd electron makes gaseous NO paramagnetic.

$$:N \overset{\cdot\cdot\cdot}{=} O:$$

N$-$O bond distance is 1·14 Å which lies in between that of double bond and triple bond. As gaseous nitric oxide donot exhibit the tendency for demerisation, it suggests that the odd electron is spread over the whole molecule. The molecule of NO may be conveniently represented as a resonance hybrid having the following two structures.

$$:\dot{N} = \ddot{O}: \leftrightarrow :\overset{-}{\ddot{N}} = \overset{+}{\dot{O}}:$$

- **Dinitrogen trioxide (N_2O_3) :**

This oxide is also called nitrogen sesquioxide. It is nitrogen III oxide as the nitrogen atom in it, is at +3 oxidation state.

Preparation : Nitrogen trioxide is prepared by distilling *60% nitric acid with* equal amount of *arseneous oxide or starch.* When nitric acid is reduced by As_2O_3 or starch to dinitrogen tri oxide. The red vapours of N_2O_3 coming out of the flask are condensed to a deep blue liquid in a receiver kept in a freezing mixture.

$$2HNO_3 + As_2O_3 + 2H_2O = 2H_3AsO_4 + N_2O_3$$

$$18HNO_3 + 2C_6H_{10}O_5 = 6C_2H_2O_4 + 9N_2O_3 + 13H_2O$$

Properties :

(i) Nitrogen trioxide is very unstable at ordinary temperature. 90% of it is decomposed to give a mixture of NO and NO_2

$$N_2O_3 = NO + NO_2$$

(ii) Nitrogen trioxide is called the anhydride of nitrous acid because it dissolves in water forming nitrous acid.

$$N_2O_3 + H_2O = 2HNO_2$$

(iii) When treated with alkali solution it produces alkali nitrites.

$$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O$$

2.19. Nitrogen dioxide $\rightleftharpoons$ Dinitrogen tetroxide [$2NO_2 \rightleftharpoons N_2O_4$]

This oxide of nitrogen is called *nitrogen (IV) oxide* since the nitrogen atom in it is in +4 oxidation state. This oxide is also called *mixed acid anhydride* as it gives both *nitrous acid and nitric acid* when treated with water.

• Preparation of nitrogen dioxide :

1. Laboratory method.

[A] **Principle :** Nitrogen dioxide is prepared in the laboratory by *heating lead nitrate.*

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

[B] **Procedure :** Powdered lead nitrate is taken in hard glass test tube fitted with a delivery tube. The test tube is clamped with a stand in slightly inclined position. The other end of the delivery tube is joined to a U-tube kept in a freezing mixture. The hard glass test tube is heated strongly when nitrogen dioxide is evolved as brown fumes along with oxygen. The evolved gas mixture passes through the U-tube where nitrogen dioxide condenses as a *yellow liquid* and oxygen passes out.

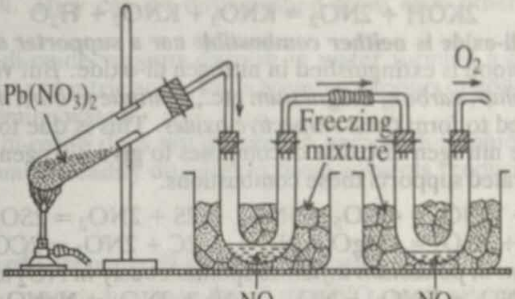


Fig 2.18 : Preparation of nitrogen dioxide

The U-tube with the yellow liquid is next kept in hot water when nitrogen dioxide evolves as reddish brown gas which is collected by the *upward displacement of air*.

2. **From nitric oxide :**

At ordinary temperature nitric oxide combines with oxygen to yield nitrogen dioxide. This is used for the large scale preparation of NO_2.

$$2NO + O_2 = 2NO_2$$

3. **From nitric acid :** (a) Conc. *HNO_3 is thermally decomposed* to give off nitrogen di-oxide when it is allowed to drop on red hot pumic stone.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

(b) Conc. HNO_3 is *reduced by copper or zinc* to produce nitrogen dioxide.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

- **Properties :**

[A] **Physical :** (i) At ordinary temperature it is a reddish brown gas having suffocating odour. (ii) Its colour gradually fades as the temperature falls. At −9°C colourless crystals of dinitrogen tetroxide are obtained. In solid form its molecular formula becomes N_2O_4. With the increase of temperature the colourless crystals are first converted to yellow liquid and then to a brown gas at 22°C. The more the temperature rises the more the colour of the gas deepens, and at 140°C it becomes deep brown. At this stage N_2O_4 molecules completely dissociate to NO_2 molecules. At above 140°C the colour of NO_2 begins to fade away as the dissociation of NO_2 begins. It begins to dissociate into colourless NO and O_2. At 620°C this dissociation of NO_2 is complete. The whole process is represented as follows—

$$\underset{\substack{\text{colourless}\\\text{crystals}}}{N_2O_4} \overset{-9^\circ C}{\rightleftharpoons} \underset{\substack{\text{yellow}\\\text{liquid}}}{N_2O_4} \overset{22^\circ C}{\rightleftharpoons} \underset{\substack{\text{brown}\\\text{vapour}}}{N_2O_4} \overset{140^\circ C}{\rightleftharpoons} \underset{\substack{\text{reddish}\\\text{brown gas}}}{2NO_2} \overset{620^\circ C}{\rightleftharpoons} \underset{\text{colourless}}{2NO + O_2}$$

(iii) Nitrogen di-oxide is soluble in water. (iv) It is heavier than air. (v) It is poisonous.

[B] **Chemical :**

(1) **Nitrogen di-oxide is an *acidic oxide*.** (a) When it is dissolved in cold water, a mixture of *nitric acid* and *nitrous acid* is obtained. This is why nitrogen di-oxide is called a *mixed anhydride of nitrous acid* and *nitric acid*.

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

(b) With hot water it produces *nitric acid* with the liberation of *nitric oxide*.

$$3NO_2 + H_2O = 2HNO_3 + NO$$

(c) It is *acidic towards litmus*. With *sodium hydroxide* or *potassium hydroxide* solution, it forms *nitrate and nitrite salts.*

$$2KOH + 2NO_2 = KNO_3 + KNO_2 + H_2O$$

(2) **Nitrogen di-oxide is *neither combustible nor a supporter of combustion* :** A burning chip of wood is extinguished in nitrogen di-oxide. But vigorously *burning phosphorus, sulphur, carbon, magnesium* etc., *continue to burn more vigorously* in it and are oxidised to form their *respective oxides.* This is due to the fact that at a high temperature nitrogen di-oxide decomposes to give nitrogen and oxygen. The oxygen thus liberated supports these combustions.

$$2P_4 + 10NO_2 = 4P_2O_5 + 5N_2, \qquad 2S + 2NO_2 = 2SO_2 + N_2$$

$$4Mg + 2NO_2 = 4MgO + N_2, \qquad 2C + 2NO_2 = 2CO_2 + N_2$$

Warmed sodium or *potassium inflames* spontaneously in NO_2 to form *nitrates.*

$$K + 2NO_2 = KNO_3 + NO, \qquad Na + 2NO_2 = NaNO_3 + NO$$

(3) **Oxidising property :** Nitrogen di-oxide exhibits remarkable oxidising property.

(i) It can oxidise *potassium iodide* solution to *free iodine* which turns starch solution blue.

$$2K\overset{-1}{I} + NO_2 + H_2O = 2KOH + \overset{0}{I_2} + NO$$

(ii) In presence of *steam,* it oxidises *sulphur dioxide* to *sulphuric acid.*

$$\overset{+4}{S}O_2 + H_2O + NO_2 = H_2\overset{+6}{S}O_4 + NO$$

The manufacture of H_2SO_4 by lead chamber process is based on the oxidation of SO_2 by NO_2 in presence of steam.

(iii) *Hydrogen sulphide* is oxidised to *free sulphur* and *carbon monoxide* to *carbon di-oxide.*

$$H_2\overset{-1}{S} + NO_2 = H_2O + NO + \overset{0}{S}\downarrow$$

$$\overset{+2}{C}O + NO_2 = \overset{+4}{C}O_2 + NO$$

(iv) Acidified ferrous sulphate is oxidised to ferric sulphate changing its colour to yellow.

$$2\overset{+2}{Fe}SO_4 + NO_2 + H_2SO_4 = \overset{+3}{Fe_2}(SO_4)_3 + H_2O + NO$$

(v) When nitrogen di-oxide is passed over strongly *heated copper,* the latter is oxidised to give black *cupric oxide.*

$$4Cu + 2NO_2 = 4CuO + N_2$$

(4) Nitrogen di-oxide is *absorbed by conc. H_2SO_4* to form *nitroso sulphuric acid.*

$$2NO_2 + H_2SO_4 = \underset{\text{Nitroso sulphuric acid}}{SO_2(OH)ONO} + HNO_3$$

(5) Nitrogen di-oxide is reduced to ammonia by hydrogen in presence of platinum catalyst.

$$2\overset{+4}{N}O_2 + 7H_2 = 2\overset{-3}{N}H_3 + 4H_2O$$

• Tests for NO_2

(i) Nitrogen di-oxide is identified by its *suffocating odour and brown colour.*

(ii) It gives a colourless solution with water and the aqueous solution thus obtained turns blue litmus red.

(iii) It is not soluble in carbon di-sulphide or carbon tetrachloride.

• Uses of NO_2 : It is used in the manufacture of nitric acid. It is also used as rocket fuel.

• *Distinction between nitrogen di-oxide and bromine :*

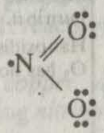
Nitrogen di-oxide and bromine vapours are both reddish brown in colour having suffocating smell. They can be distinguished from each other by the following methods :—

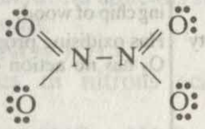
(i) Nitrogen di-oxide vapours dissolve in water forming a colourless solution containing nitrous and nitric acids, while bromine vapours dissolve in water forming red coloured bromine water.

(ii) Nitrogen di-oxide does not dissolve in carbon di-sulphide or carbon tetrachloride but bromine readily dissolves in these solvents producing a red coloured solution.

• Structure of nitrogen di-oxide molecule.

From different tests it has been found that NO_2 molecule is not linear but 'V' shaped structure having O—N—O bond angle = 132° and N—O bond distance = 1·19Å NO_2 is an odd molecule. This structure goes to show that it has an unpaired electron and hence it is *paramagnetic.* Consequently it has tendency to demerise to colourless N_2O_4 molecule, which is planer with N—N bond distance = 1·75Å and O—N—O bond angle = 132°. In this molecule there is no unpaired electron and so it is *dimagnetic.*





2.20. Dinitrogen pentoxide (N_2O_5).

This is nitrogen (V) oxide since the nitrogen atom is in +5 oxidation state in this oxide.

• Preparation.

(i) Nitrogen pentoxide is prepared by gently heating concentrated *nitric acid* with *phosphorus pentoxide* when nitric acid is dehydrated by P_2O_5 to form nitrogen pentoxide. The vapours of N_2O_5 come out and condense in ice cold receiver as colourless shining crystals.

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$$

(ii) Nitrogen pentoxide is also prepared by the action of *ozone* on *dinitrogen tetroxide.*

$$N_2O_4 + O_3 = N_2O_5 + O_2$$

Properties :

(i) In solid state it is colourless shining crystal which melts at 30°C.

(ii) It is unstable and has tendency to decompose to N_2O_4 and O_2.

(iii) It acts vigorously with water with the formation of nitric acid.

It is called *anhydride of nitric acid* as this oxide is produced by extracting one molecule of water from two molecules of nitric acid.

$$N_2O_5 \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} 2HNO_3$$

(iv) It has *oxidising property*. It oxidises iodine to iodine pentoxide.

$$I_2 + 5N_2O_5 = I_2O_5 + 10NO_2$$

• Comparison of the three oxides of nitrogen—N_2O, NO and N_2O_4 •

Properties	Nitrous oxide (N_2O)	Nitric (NO)	Nitrogen di-oxide (NO_2)
1. Physical state	Colourless gas at ordinary temperature.	Colourless gas at ordinary temperature.	Reddish brown gas at ordinary temperature.
2. Odour	It has a faint pleasant smell—causes hysteric laughter.	It is not possible to describe its smell as in contact with air it turns to NO_2.	It has a suffocating smell.
3. Vapour density	Vapour density = 22 about 1·5 times heavier than air.	V.D. = 15. heavier than air.	V.D. = 23. about 1·6 times heavier than air.
4. Solubility	Fairly soluble in cold water.	Almost insoluble in water.	highly soluble in water.
5. Nature	Neutral oxide.	Neutral oxide.	Acidic oxide.
6. Action on alkali.	Does not react with alkali.	Does not react with alkali.	Reacts with alkali to form nitrate and nitrite salts.
7. Combustibility	Non-combustible but a supporter of combustion. It supports combustion most vigorously, can rekindle a glowing chip of wood.	Non combustible. It extinguishes a burning splinter or a candle but supports the combustion of burning P.S. Mg etc.	Non-combustible. A burning candle or splinter is extinguished in it, but burning P.S. Mg etc., continues to burn in it.
8. Oxidising property	Has oxidising property.	Has oxidising property.	Has oxidising property.
9. Action on O_2	O_2 has no action on it.	O_2 produces brown fumes of NO_2 when comes in contact with it.	O_2 has no action on it.
10. Reduction	Reduced to N_2 by hot metals like Cu, Mg.	Reduced to N_2 by hot Cu, Mg.	Reduced to N_2 by hot metals like Cu.
11. Absorbants	Absorbed by alcohol.	Absorbed by freshly prepared ferrous sulphate solution.	Absorbed by KOH or NaOH solution.
12. Physiological action	Poisonous—causes hysteric laughter when inhaled in small quantity.	Poisonous.	Poisonous.

• Oxyacids of nitrogen •

Nitrogen forms a number of oxyacids of which (i) *Nitrous acid* and (ii) *Nitric acid* are of importance.

2.21. Nitrous acid (HNO_2).

Molecular wt. = 47 Equivalent wt. = 47

Nitrous acid is very unstable and can exists only in solution.

• Preparation :

Laboratory method :

[A] **Principle :** In the laboratory nitrous acid is prepared by the action of *ice cold solution of barium nitrite* on *dilute sulphuric acid.*

$$Ba(NO_2)_2 + H_2SO_4 = BaSO_4 \downarrow + 2HNO_2$$

[B] **Procedure :** (i) Barium nitrite solution is taken in a beaker and kept on ice. Now a calculated quantity of ice cold dilute sulphuric acid is added to the cold barium nitrite solution with constant stirring. Insoluble barium sulphate and nitrous acid are produced. On the completion of the reaction the white precipitate of $BaSO_4$ is separated by filtration. An aqueous solution of nitrous acid is obtained as a clear filtrate.

(ii) An aqueous solution of nitrous acid can be obtained by treating an ice cold solution of *sodium nitrite* or *potassium nitrite with dilute hydrochloric acid* or *sulphuric acid.*

$$NaNO_2 + HCl = HNO_2 + NaCl$$
$$KNO_2 + H_2SO_4 = HNO_2 + KHSO_4$$

(iii) *Nitrogen trioxide* on treatment with ice cold water yields nitrous acid.

$$N_2O_3 + H_2O = 2HNO_2$$

[C] **Properties :** (i) Nitrous acid is very *unstable* even at ordinary temperatures. In its aqueous solution it decomposes to *nitric acid* and *nitric oxide.*

$$3H\overset{+3}{N}O_2 = H\overset{+5}{N}O_3 + 2\overset{+2}{N}O + H_2O$$

[This reaction is an example of **disportionation.** In such type of reaction, an element in an intermediate oxidation state is converted to a mixture of lower and higher oxidation state, e.g., in this reaction the oxidation state of nitrogen atom in HNO_2 is +3. After the reaction it is converted to +5 in HNO_3 and +2 in NO. Thus HNO_2 is partly oxidised to HNO_3 and partly reduced to NO.]

At higher temperature it decomposes to nitrogen di-oxide and nitric oxide.

$$2HNO_2 = NO_2 + NO + H_2O$$

(ii) **Acid property :** It is a weak monobasic acid. Its aqueous solution turns blue litmus red. It reacts with *alkalis* to form *nitrite salts.*

$$NaOH + HNO_2 = NaNO_2 + H_2O$$

Metallic copper or silver slowly dissolves in nitrous acid forming their corresponding *nitrites.*

$$Cu + 4HNO_2 = Cu(NO_2)_2 + 2NO + 2H_2O$$
$$Ag + 2HNO_2 = AgNO_2 + NO + H_2O$$

(iii) **Oxidising property :**

(a) Nitrous acid oxidises *acidified potassium iodide* solution to free *iodine* and thus the clear solution turns brown.

$$\begin{array}{c} 2HNO_2 = H_2O + 2NO + O \\ 2KI + O = K_2O + I_2 \\ K_2O + 2HCl = 2KCl + H_2O \\ \hline 2H\overset{+3}{N}O_2 + 2K\overset{-1}{I} + 2HCl = 2KCl + \overset{0}{I_2} + 2\overset{+2}{N}O + 2H_2O \end{array}$$

(b) *Acidified stannous salts* are oxidised to *stannic salts.*

$$\begin{array}{c} 2HNO_2 = H_2O + 2NO + O \\ SnCl_2 + 2HCl + O = SnCl_4 + H_2O \\ \hline \overset{+2}{Sn}Cl_2 + 2H\overset{+3}{N}O_2 + 2HCl = \overset{+4}{Sn}Cl_4 + 2\overset{+2}{N}O + 2H_2O \end{array}$$

(c) *Hydrogen sulphide* is oxidised to free *sulphur.*

$$\begin{array}{c} 2HNO_2 = H_2O + 2NO + O \\ H_2S + O = H_2O + S \\ \hline 2H\overset{+3}{N}O_2 + H_2\overset{-2}{S} = 2\overset{+2}{N}O + \overset{0}{S}\downarrow + 2H_2O \end{array}$$

(d) *Sulphur di-oxide* is oxidised to *sulphuric acid.*

$$\begin{array}{c} 2HNO_2 = H_2O + 2NO + O \\ SO_2 + O = SO_3 \\ SO_3 + H_2O = H_2SO_4 \\ \hline 2H\overset{+3}{N}O_2 + \overset{+4}{S}O_2 = H_2\overset{+6}{S}O_4 + 2\overset{+2}{N}O \end{array}$$

(e) *Acidified ferrous salts are oxidised* to yellow coloured *ferric salts*. Thus acidified ferrous sulphate is oxidised by HNO_2 to ferric sulphate.

$$\begin{array}{c}
2HNO_2 = H_2O + 2NO + O \\
2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O \\
\hline
2\overset{+2}{Fe}SO_4 + 2H\overset{+3}{N}O_2 + H_2SO_4 = \overset{+3}{Fe}_2(SO_4)_3 + 2\overset{+2}{N}O + 2H_2O
\end{array}$$

(iv) **Reducing property :** Nitrous acid possesses *reducing property also*, as it is capable of being oxidised to nitric acid by accepting an oxygen atom from other substances.

(a) It reduces *red coloured bromine* water to colourless *hydrobromic acid*.

$$\overset{0}{Br}_2 + H\overset{+3}{N}O_2 + H_2O = 2H\overset{-1}{Br} + H\overset{+5}{N}O_3$$

(b) When *chlorine* is passed through nitrous acid, it is reduced to *hydrochloric acid*.

$$\overset{0}{Cl}_2 + H\overset{+3}{N}O_2 + H_2O = 2H\overset{-1}{Cl} + H\overset{+5}{N}O_3$$

(c) *Hydrogen peroxide* is reduced to *water*.

$$H_2\overset{-1}{O}_2 + H\overset{+3}{N}O_2 = H\overset{+5}{N}O_3 + H_2\overset{-2}{O}$$

(d) Nitrous acid decolourises the violet colour of *acidified potassium permanganate* solution by reducing it to colourless *manganous salts*.

$$\begin{array}{c}
2KMnO_4 = K_2O + 2MnO + 5O \\
5HNO_2 + 5O = 5HNO_3 \\
K_2O + H_2SO_4 = K_2SO_4 + H_2O \\
2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O \\
\hline
2K\overset{+7}{Mn}O_4 + 5H\overset{+3}{N}O_2 + 3H_2SO_4 = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 5H\overset{+5}{N}O_3 + 3H_2O
\end{array}$$

It reduces acidified $K_2Cr_2O_7$ to chromic salt and thus the colour of the solution turns green form orange.

$$K_2\overset{+6}{Cr}_2O_7 + 4H_2SO_4 + 3HNO_2 = K_2SO_4 + \overset{+3}{Cr}_2(SO_4)_3 + 3HNO_3 + 4H_2O$$

(v) Nitrous acid reacts with *ammonia* or *ammonium salts* or *organic compounds containing —NH_2 group* with the evolution of *nitrogen*.

$$\begin{array}{llll}
NH_3 + HNO_2 & = N_2 & + 2H_2O & \\
NH_4Cl + HNO_2 & = N_2 & + 2H_2O & + HCl \\
CH_3NH_2 + HNO_2 & = CH_3OH & + N_2 & + H_2O
\end{array}$$

• Nitrous acid possesses both the oxidising and the reducing properties—Explain why.

Nitrous acid can act both as an oxidising agent as well as a reducing agent. This is because of the fact that the nitrogen atom in nitrous acid is in +3 oxidation state. The next higher oxidation state of N-atom is +5 as in HNO_3 and the next lower oxidation state of N atom is +2 as in NO. So the nitrogen atom of HNO_2 has the scope to increase its oxidation number from +3 to +5 or has the scope to decrease its oxidation number from +3 to +2

$$\overset{+2}{N}O,\quad H\overset{+3}{N}O_2,\quad H\overset{+5}{N}O_3.$$

(a) Now when the N atom of HNO_2 increases its oxidation number from +3 to +5, it is oxidised and this oxidation is brought out by reducing the other substance. Under this condition, HNO_2 exhibits reducing property. Thus when nitrous acid is treated with H_2O_2, nitrous acid collects O-atom from H_2O_2 to form nitric acid and thus oxidised and this oxidation is carried out by reducing H_2O_2 to water.

$$\begin{array}{c} H_2O_2 = H_2O + O \\ HNO_2 + O = HNO_3 \\ \hline \overset{+3}{HNO_2} + H_2\overset{-1}{O_2} = H\overset{+5}{N}O_3 + H_2\overset{-2}{O} \end{array}$$

(b) When the N-atom of HNO_2 decreases its oxidation number from +3 to +2, it is reduced and this reduction is brought out by oxidising the others. At this stage HNO_2 donates oxygen atom to others, itself being reduced to nitric oxide and thus exhibits oxidising property.

As for example, when H_2S is passed through HNO_2, H_2S is oxidised to free sulphur and HNO_2 is reduced to nitric oxide.

$$\begin{array}{c} 2HNO_2 = H_2O + 2NO + O \\ H_2S + O = H_2O + S \\ \hline 2H\overset{+3}{N}O_2 + H_2\overset{-2}{S} = 2H_2O + \overset{0}{S} + 2\overset{+2}{N}O \end{array}$$

- **Tests for nitrous acid :**

(i) When nitrous acid is treated with acidified solution of potassium iodide, the clear solution of KI turns brown due to the liberation of free iodine. The liberated iodine may be identified by the formation of deep blue colour on its treatment with starch solution.

$$KI + 2HNO_2 + 2HCl = 2KCl + 2NO + I_2 + 2H_2O$$
$$I_2 + \text{Starch solution} \rightarrow \text{blue colour}$$

(ii) Nitrous acid decolourises the pink colour of acidified solution of potassium permanganate.

$$\underset{\text{Violet colour}}{2KMnO_4} + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + \underset{\text{Colourless}}{2MnSO_4} + 5HNO_3 + 3H_2O$$

(iii) Brown fumes are evolved when nitrous acid is heated

$$2HNO_2 = H_2O + NO_2 + NO$$

- **Uses of nitrous acid :** (i) Nitrous acid is used for the detection of amino group ($-NH_2$) in organic compounds. (ii) It is used for the preparation of *diazonium* compounds and in *coupling reaction*. (iii) It has also its use in the preparation of *azodyes*.

- **Structure :** The molecular structure of nitrous acid is given below—

$$H \,:\, \underset{\bullet\bullet}{\ddot{O}} \,:\, \overset{\circ\circ}{N} \,::\, \ddot{O}: \rightarrow H - \underset{\bullet\bullet}{\ddot{O}} - \overset{\circ\circ}{N} = \ddot{O}:$$

2.22. Nitric acid (HNO_3).

Mol wt.—63	**Equivalent wt.—63**

The use of nitric acid was known to the alchemists who called it '*aqua fortis*'. Geber (778 A.D.) was the first to obtain this acid by distilling a mixture of *nitre, blue vitriol* and *alum*. Glauber (1648) obtained this acid by distilling nitre with concentrated sulphuric acid.

Traces of nitric acid is found to be present in the atmosphere. It is also found in the form of *nitre* in the soils of tropical countries and as *saltpetre* in Chile.

- **Preparation of nitric acid :**

Laboratory method.

[A] **Principle :** Nitric acid is far more volatile than sulphuric acid. Consequently it is prepared in the laboratory by heating *potassium nitrate* or *sodium nitrate* with *concentrated sulphuric acid*. The reaction takes place in two steps.

First step : At 200°C—300°C potassium nitrate reacts with conc. H_2SO_4 forming *potassium hydrogen sulphate* and *nitric acid.*

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$

Second step : At 800°C, the produced potassium hydrogen sulphate reacts with unreacted potassium nitrate producing more *nitric acid* and *potassium sulphate.*

$$KNO_3 + KHSO_4 = K_2SO_4 + HNO_3$$

[B] **Procedure :** Equal parts by weight of potassium nitrate and conc. H_2SO_4 are taken in a glass retort the end of which is introduced into a round bottomed flask which acts as the receiver. The flask is kept floating on cold water and is cooled by running water. The retort is placed on a wire gauze and is clamped to a stand. The retort is then heated gently to about 200°C. Reaction takes place and nitric acid vapours evolve. The vapours thus produced pass on and enter into the water cooled receiver and condense as a slight yellowish liquid.

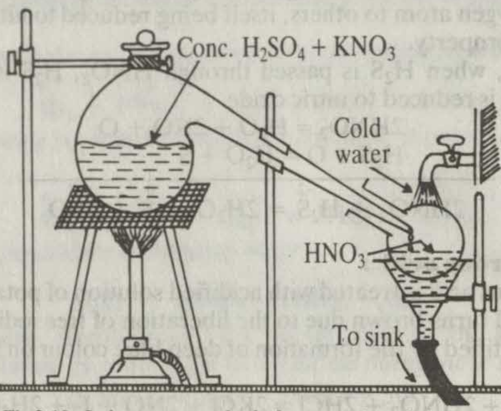


Fig 2.19 : Laboratory method of preparation of nitric acid

[C] **Purification :** The nitric acid thus prepared in the laboratory is not pure. It contains *moisture* and dissolved *nitrogen di-oxide.*

(i) It is distilled with conc. H_2SO_4 at low pressure when water is removed.

(ii) Air is then bubbled at 70°C through the acid till it becomes colourless. The dissolved nitrogen di-oxide is thus removed from the acid. The product thus obtained is 98% pure. Pure nitric acid may be obtained as colourless crystals on cooling the 98% acid to −42°C.

• Nitric acid obtained by the laboratory method is slightly yellowish —Explain why.

The nitric acid obtained by the laboratory method is slightly yellowish due to the presence of dissolved nitrogen di-oxide in it which comes from the thermal decomposition of the produced nitric acid.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

• Hydrochloric acid is not used in the preparation of nitric acid—Explain why.

The boiling point of sulphuric acid (338°C) is much higher than that of nitric acid (86°C). Thus conc. H_2SO_4 is much less volatile than nitric acid. Consequently it is more conveniently used to expel the more volatile nitric acid from a nitrate.

Nitric acid is not produced by heating hydrochloric acid with nitrate salts. It is due to the fact that hydrochloric acid is more volatile than nitric acid. Thus when HCl is heated with a nitrate, most of HCl distills along with some HNO_3 vapour and are collected in the receiver. Moreover the produced HNO_3 reacts with HCl yielding nitrosyl chloride with the evolution of Cl_2.

$$3HCl + HNO_3 = NOCl + Cl_2 + 2H_2O$$

This is why HCl is not used in the preparation of HNO_3 in the laboratory.

• In the laboratory method of preparation of HNO_3 the temperature is not allowed to exceed 200°C—Explain why.

If the mixture of potassium nitrate and conc. H_2SO_4 is heated above 200°C, the produced potassium hydrogen sulphate reacts with the unreacted KNO_3 producing more HNO_3. But the temperature is not allowed to exceed 300°C because of the fact that—(i) the nitric acid produced by the reaction is thermally decomposed at this high temperature to nitrogen di-oxide and oxygen.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

(ii) The potassium hydrogen sulphate which is produced in the first step of the reaction at 200°C, remains in molten state and so can easily be removed from the retort. But at a higher temperature, potassium sulphate is produced which remains in the solid state and sticks to the walls of the retort and so cannot easily be removed from the retort.

(iii) At higher temperatures nitric acid vapours attacks the materials of the glass retort.

• **Fuming nitric acid :** It is produced by distilling conc. HNO_3 with a *little starch.* Some of the acid is reduced by starch to nitrogen di-oxide and N_2O_3 which dissolve in the remaining nitric acid to form fuming nitric acid. Due to the presence of dissolved oxides of nitrogen (NO_2, N_2O_3) its colour becomes yellow. *Fuming nitric acid is more powerful oxidising agent and nitrating agent than conc. HNO_3.*

• Properties of nitric acid :

[A] **Physical :** (i) Pure nitric acid is a colourless fuming liquid with a suffocating smell. It boils at 86°C and freezes at −42°C. It is highly soluble in water.

[B] **Chemical :**

(1) ***Action of heat :*** Nitric acid is completely decomposed on heating yielding oxygen, steam and nitrogen di-oxide.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

Even in sunlight, nitric acid is decomposed to give nitrogen dioxide which dissolves in the acid to give it a yellow colour.

(2) ***Acid property :*** Nitric acid is a strong monobasic acid. It ionises almost completely to nitrate ions (NO_3^-) and hydrogen ions (hydroxonium H_3O^+)

$$HNO_3 \rightleftharpoons H^+ + NO_3^- \qquad H_2O + H^+ \rightleftharpoons H_3O^+$$

As nitric acid is monobasic, it forms normal salts (*nitrates*) only.

It turns blue litmus red.

(a) It reacts with *basic oxides* and *hydroxides* producing *nitrate salts* and *water.*

$$CaO + 2HNO_3 = Ca(NO_3)_2 + H_2O$$
$$MgO + 2HNO_3 = Mg(NO_3)_2 + H_2O$$
$$ZnO + 2HNO_3 = Zn(NO_3)_2 + H_2O$$
$$NaOH + HNO_3 = NaNO_3 + H_2O$$

(b) It reacts with *metallic carbonates* or *bicarbonates* producing *nitrates* and *liberating CO_2.*

$$Na_2CO_3 + 2HNO_3 = 2NaNO_3 + CO_2 + H_2O$$
$$CuCO_3 + 2HNO_3 = Cu(NO_3)_2 + CO_2 + H_2O$$
$$NaHCO_3 + HNO_3 = NaNO_3 + CO_2 + H_2O$$

(c) *Very dilute nitric acid reacts with magnesium and manganese in cold yielding magnesium nitrate liberating hydrogen.*

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2\uparrow$$

- *The metals which are above hydrogen in the electro-chemical series (Zn, Fe, etc.) fail to liberate hydrogen.* This is due to the fact that though nitric acid liberates H_2 due to its acid property when reacted with these metals, but the liberated hydrogen is oxidised to water due to the oxidising property of nitric acid.

$$\begin{aligned} &Zn + 2HNO_3 = Zn(NO_3)_2 + 2H \\ &2HNO_3 = H_2O + 2NO_2 + O \\ &2H + O = H_2O \\ \hline &Zn + 4HNO_3 = Zn(NO_3)_2 + 2NO_2 + 2H_2O \end{aligned}$$

(3) ***Oxidising property :***

Nitric acid is a strong oxidising agent. It decomposes easily to oxides of nitrogen liberating nascent oxygen. This liberated nascent oxygen oxidises metals, non-metals and various compounds.

- **Nitric acid has oxidising power only and has no reducing power—Explain why :**

The oxidation number of nitrogen atom in nitric acid is +5. This is the highest oxidation state which is exhibited by nitrogen. So there is no scope for the N-atom of nitric acid to increase its oxidation state i.e., it has no scope to be oxidised by reducing others. Consequently nitric acid has no reducing property.

On the other hand nitrogen atom of HNO_3 has enough scope to reduce its oxidation state from +5 to +4, +3, +2, +1 or 0. Thus it can easily be reduced by decreasing its oxidation number. Now reduction cannot occur without the oxidation of others. So the N-atom of HNO_3, oxidises other substances, itself being reduced to $\overset{+4}{NO_2}$, $\overset{+2}{NO}$, $\overset{+1}{N_2O}$ or, $\overset{0}{N_2}$. As an oxidising agent HNO_3 is liable to be reduced successively as—

$$\overset{+5}{HNO_3} \rightarrow \overset{+4}{NO_2} \rightarrow \overset{+2}{NO} \rightarrow \overset{+1}{N_2O} \rightarrow \overset{0}{N_2}$$

The extent of reduction being determined by the conditions of the reaction.

[I] **Oxidation of non metals :**

Most of the non metals when heated with concentrated nitric acid, are oxidised to oxides or oxyacids.

(i) Burning *carbon* is oxidised by conc. HNO_3 to *carbon di-oxide* and *silicon* is oxidised to *silica.*

$$\begin{aligned} &(2HNO_3 = H_2O + 2NO_2 + O) \times 2 \\ &C + 2O = CO_2 \\ \hline &\overset{0}{C} + 4HNO_3 = \overset{+4}{CO_2} + 4NO_2 + 2H_2O \end{aligned}$$

$$\begin{aligned} &(2HNO_3 = H_2O + 2NO_2 + O) \times 2 \\ &Si + 2O = SiO_2 \\ \hline &4HNO_3 + \overset{0}{Si} = \overset{+4}{SiO_2} + 4NO_2 + 2H_2O \end{aligned}$$

(ii) *Phosphorus* is oxidised *by hot and conc. HNO_3* to phosphoric acid, nitric acid being reduced to *nitric oxide* and *nitrogen di-oxide.*

$$\begin{aligned} &(2HNO_3 = H_2O + NO + NO_2 + 2O) \times 5 \\ &4P + 10O = 2P_2O_5 \\ &2P_2O_5 + 6H_2O = 4H_3PO_4 \\ \hline &\overset{0}{4P} + 10H\overset{+5}{N}O_3 + H_2O = 4H_3\overset{+5}{P}O_4 + 5\overset{+2}{N}O + 5\overset{+4}{N}O_2 \end{aligned}$$

(iii) *Iodine* is oxidised to *iodic acid by hot* and *conc.* HNO_3

$$\begin{array}{l} (2HNO_3 = H_2O + 2NO_2 + O) \times 5 \\ I_2 + 5O = I_2O_5 \\ I_2O_5 + H_2O = 2HIO_3 \\ \hline \end{array}$$

$$\overset{0}{I_2} + 10HNO_3 = 2H\overset{+5}{I}O_3 + 10NO_2 + 4H_2O$$

(iv) *Hot and conc.* HNO_3 oxidises *sulphur* to *sulphuric acid.*

$$\begin{array}{l} (2HNO_3 = H_2O + 2NO_2 + O) \times 3 \\ S + 3O = SO_3 \\ SO_3 + H_2O = H_2SO_4 \\ \hline \end{array}$$

$$6HNO_3 + \overset{0}{S} = H_2\overset{+6}{S}O_4 + 6NO_2 + 2H_2O$$

Chlorine, bromine, nitrogen, oxygen are not attacked by nitric acid.

[II] Oxidation of inorganic compounds :

Moderately concentrated HNO_3 or even hot and dilute HNO_3 oxidises many inorganic compounds, itself being reduced to *nitric oxide.*

(i) *Hydrobromic acid* and *hydroiodic acid* are oxidised by nitric acid to *bromine* (red) and *iodine* (brown) respectively.

$$\begin{array}{l} 2HNO_3 = H_2O + 2NO + 3O \\ 6HBr + 3O = 3H_2O + 3Br_2 \\ \hline \end{array}$$

$$2H\overset{+5}{N}O_3 + 6H\overset{-1}{Br} = 3\overset{0}{Br_2} + 2\overset{+2}{N}O + 4H_2O$$

Similarly, $2HNO_3 + 6HI = 3I_2 + 2NO + 4H_2O$

(ii) *Bromides* and *iodides* are oxides to *bromine* and *iodine* respectively.

$$\begin{array}{l} 2HNO_3 = H_2O + 2NO + 3O \\ 6KBr + 3O = 3K_2O + 3Br_2 \\ 3K_2O + 6HNO_3 = 6KNO_3 + 3H_2O \\ \hline \end{array}$$

$$6K\overset{-1}{Br} + 8H\overset{+5}{N}O_3 = 6KNO_3 + 3\overset{0}{Br_2} + 2\overset{+2}{N}O + 4H_2O$$

Similarly, $6K\overset{-1}{I} + 8H\overset{+5}{N}O_3 = 6KNO_3 + 3\overset{0}{I_2} + 2\overset{+2}{N}O + 4H_2O$

(iii) *Sulphur di-oxide is oxidised to sulphuric acid* by conc. HNO_3 with the evolution of brown fumes of nitrogen dioxide.

$$\begin{array}{l} 2HNO_3 = H_2O + 2NO_2 + O \\ SO_2 + O = SO_3 \\ SO_3 + H_2O = H_2SO_4 \\ \hline \end{array}$$

$$\overset{+4}{S}O_2 + 2H\overset{+5}{N}O_3 = H_2\overset{+6}{S}O_4 + 2\overset{+4}{N}O_2$$

(iv) *Hydrogen sulphide* is oxidised to *free sulphur* and a yellow precipitate of sulphur is obtained.

$$\begin{array}{l} 2HNO_3 = H_2O + 2NO + 3O \\ 3H_2S + 3O = 3H_2O + 3S \\ \hline \end{array}$$

$$3H_2\overset{-2}{S} + 2HNO_3 = 2NO + 3\overset{0}{S}\downarrow + 4H_2O$$

Hydrogen sulphide may further be oxidised to sulphuric acid.

$$H_2S + 8HNO_3 = H_2SO_4 + 8NO_2 + 4H_2O$$

(v) An acidified colourless solution of *ferrous sulphate* is oxidised to give a yellow solution of *ferric sulphate.*

$$\begin{array}{c} 2HNO_3 = H_2O + 2NO + 3O \\ [2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O] \times 3 \\ \hline 2H\overset{+5}{N}O_3 + 6\overset{+2}{Fe}SO_4 + 3H_2SO_4 = 3\overset{+3}{Fe_2}(SO_4)_3 + 2\overset{+2}{N}O + 4H_2O \end{array}$$

Similarly ferrous chloride solution is oxidised to ferric chloride.

$$\begin{array}{c} 2HNO_3 = H_2O + 2NO + 3O \\ (2FeCl_2 + 2HCl + O = 2FeCl_3 + H_2O) \times 3 \\ \hline 2HNO_3 + 6FeCl_2 + 6HCl = 6FeCl_3 + 2NO + 4H_2O \end{array}$$

[III] **The oxidation of metals :**

The way of reaction between nitric acid and metals is not simple. In the reactions with metals, nitric acid plays a double role—acting simultaneously as (i) an acid and (ii) an oxidising agent.

(a) *Action of nitric acid on metals which are above hydrogen in the electrochemical series :*

Due to its acid property metals like magnesium, zinc, iron etc., which are above hydrogen in the electrochemical series initially react with HNO_3 liberating nascent hydrogen. This nascent hydrogen then reduces the rest of nitric acid to give different oxides of nitrogen or ammonia, depending on the concentration of the acid and the nature of the metals. The degree of reduction increases with the increase of dilution of the acid.

Nitric acid is reduced by the liberated nascent hydrogen as given below—

(i) *Hot and concentrated* : $2HNO_3 + 2H \rightarrow 2NO_2 + 2H_2O$
(ii) *Moderately strong* (1 : 1) : $2HNO_3 + 6H \rightarrow 2NO + 4H_2O$
(iii) *Cold and dilute* : $2HNO_3 + 8H \rightarrow N_2O + 5H_2O$
(iv) *Very dilute* : $2HNO_3 + 16H \rightarrow 2NH_3 + 6H_2O$

(b) *Action of nitric acid on metals which are below hydrogen in the electro-chemical series.*

Metals like copper, silver, mercury etc., which are below hydrogen in the electrochemical series are unable to displace hydrogen from nitric acid. During the action with nitric acid, these metals are first oxidised by nitric acid producing the corresponding oxides, which react with the rest of the acid yielding the respective nitrates. Nitric acid on the other hand is reduced to give different oxides of nitrogen even to give free nitrogen.

Thus it is clear that the nature of the products obtained by the action of metals with nitric acid depends upon—

(i) *Concentration of the acid,*
(ii) *Temperature of the reaction,*
(iii) *Electro-chemical nature of the metals,*
(iv) *The products of the reaction.*

It is to be noted that (i) noble metals like *gold, platinum* etc., do not react with nitric acid. (ii) Metals like *iron, chromium, nickel,* do not react with concentrated nitric acid as they *are rendered passive* when come in contact with the acid. (iii) *Magnesium* and *manganese can liberate hydrogen from* very dilute nitric acid. (iv) *Aluminium is scarcely attacked* by cold nitric acid. (v) *Tin and anitmony* are converted to their respective *oxides* by nitric acid.

[A] Actions on metals which are above hydrogen in the electro-chemical series :

(1) ***Action on zinc :***

(a) Metallic zinc reacts with *hot and concentrated nitric acid* to produce *zinc nitrate* and *brown fumes of nitrogen di-oxide.*

$$\begin{array}{llllll}
Zn & +2HNO_3 & = Zn(NO_3)_2 & +2H & & \\
 & 2HNO_3 & = H_2O & +2NO_2 & +O & \\
 & 2H & +O & = H_2O & & \\
\hline
\overset{0}{Zn} & +4HNO_3 & = \overset{+2}{Zn}(NO_3)_2 & +2NO_2 & +2H_2O &
\end{array}$$

(b) *Cold and moderately strong (1 : 1) nitric acid* reacts with zinc to produce zinc nitrate and colourless *nitric oxide.*

$$\begin{array}{llllll}
[Zn & +2HNO_3 & = Zn(NO_3)_2 & +2H] & \times 3 & \\
 & 2HNO_3 & = H_2O & +2NO & +3O & \\
 & 6H & +3O & = 3H_2O & & \\
\hline
3\overset{0}{Zn} & +8HNO_3 & = 3\overset{+2}{Zn}(NO_3)_2 & +2NO & +4H_2O &
\end{array}$$

(c) *Cold and dilute nitric acid* reacts with zinc to form *zinc nitrate* and colourless *nitrous oxide.*

$$\begin{array}{llllll}
[Zn & + & 2HNO_3 & = Zn(NO_3)_2 & +2H] & \times 4 \\
 & & 2HNO_3 & = H_2O & +N_2O & +4O \\
 & & 8H & +4O & = 4H_2O & \\
\hline
4\overset{0}{Zn} & + & 10HNO_3 & = 4\overset{+2}{Zn}(NO_3)_2 & +N_2O & +5H_2O
\end{array}$$

(d) *Cold and very dilute nitric acid* reacts with zinc yielding *nitrate* and *ammonium nitrate.*

$$\begin{array}{llllll}
[Zn & + & 2HNO_3 & = Zn(NO_3)_2 & +2H] & \times 4 \\
HNO_3 & + & 8H & = NH_3 & +3H_2O & \\
HNO_3 & + & NH_3 & = NH_4NO_3 & & \\
\hline
4Zn & + & 10HNO_3 & = 4Zn(NO_3)_2 & +NH_4NO_3 & +3H_2O
\end{array}$$

(2) ***Action on magnesium :***

(a) Magnesium on being treated with *cold and moderately strong* (1 : 1) nitric acid yields *magnesium nitrate* and *nitric oxide.*

$$\begin{array}{llllll}
[Mg & +2HNO_3 & = Mg(NO_3)_2 & +2H] & \times 3 & \\
 & 2HNO_3 & = H_2O & +2NO_2 & +3O & \\
6H & +3O & = 3H_2O & & & \\
\hline
3Mg & +8HNO_3 & = 3Mg(NO_3)_2 & +2NO & +4H_2O &
\end{array}$$

(b) *Cold and very dilute nitric acid* reacts with magnesium with the formation of *nitrate* and *hydrogen.*

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$$

(3) ***Action on iron :***

(a) *Concentrated nitric acid or fuming nitric acid does not dissolve iron but renders it passive.*

Chromium and nickel are also rendered passive similarly.

A piece of iron when treated with dil. HCl or H_2SO_4 evolves H_2. It precipitates metallic Cu from copper sulphate. But if the same piece of iron be kept in conc. HNO_3 for some time and then reacted with dil. HCl or H_2SO_4 it remains unattacked. It can not displace Cu from $CuSO_4$ solution. Thus on treatment with conc. HNO_3 iron is rendered inert or passive. This phenomenon is known as *passivity*.

The passivity is apparently due to the formation of an invisible and impermeable thin film of oxide (Fe_2O_3, Cr_2O_3) on the surface of the metal which protects it from further action of the acid.

(b) *Hot and dilute nitric acid* or *moderately strong nitric acid* gives *ferric nitrate* and *nitric oxide.*

$$\begin{aligned} & 2HNO_3 &&= H_2O &&+ 2NO &&+ 3O \\ 2Fe & + 6HNO_3 &&= 2Fe(NO_3)_3 &&+ 6H && \\ 6H & + 3O &&= 3H_2O && && \\ \hline 2Fe & + 8HNO_3 &&= 2Fe(NO_3)_3 &&+ 2NO &&+ 4H_2O \\ \text{or} \quad Fe & + 4HNO_3 &&= Fe(NO_3)_3 &&+ NO &&+ 2H_2O \end{aligned}$$

(c) *Cold and dilute nitric acid* reacts with iron forming *ferrous nitrate.*

$$\begin{aligned} [Fe & + 2HNO_3 &&= Fe(NO_3)_2 &&+ 2H] \times 4 \\ HNO_3 & + 8H &&= NH_3 &&+ 3H_2O \\ HNO_3 & + NH_3 &&= NH_4NO_3 && \\ \hline 4Fe & + 10HNO_3 &&= 4Fe(NO_3)_2 &&+ NH_4NO_3 + 3H_2O \end{aligned}$$

(4) ***Action on tin :***

(i) *Cold and dilute nitric acid* reacts with tin forming *stannous nitrate* and *ammonium nitrate.*

$$\begin{aligned} [Sn & + 2HNO_3 &&= Sn(NO_3)_2 &&+ 2H] \times 4 \\ HNO_3 & + 8H &&= NH_3 &&+ 3H_2O \\ HNO_3 & + NH_3 &&= NH_4NO_3 && \\ \hline 4Sn & + 10HNO_3 &&= Sn(NO_3)_2 &&+ NH_4NO_3 + 3H_2O \end{aligned}$$

(ii) *Hot and conc. HNO_3* reacts with tin producing *stannic nitrate* which on hydrolysis produces *meta stannic acid.*

$$Sn + 4HNO_3 = H_2SnO_3 + 4NO_2 + H_2O$$

[B] Action of nitric acid on metals which are less electropositive than hydrogen.

(1) ***Action on copper :***

(a) *Hot and conc. HNO_3* reacts with copper producing *cupric nitrate* and *nitrogen di-oxide* (brown fumes).

$$\begin{aligned} & 2HNO_3 &&= H_2O &&+ 2NO_2 &&+ O \\ Cu & + O &&= CuO && && \\ CuO & + 2HNO_3 &&= Cu(NO_3)_2 &&+ H_2O && \\ \hline \overset{0}{Cu} & + 4HNO_3 &&= \overset{+2}{Cu}(NO_3)_2 &&+ 2NO_2 &&+ 2H_2O \end{aligned}$$

(b) *Cold and moderately strong (1 : 1) nitric acid* reacts with copper yielding *cupric nitrate* and *nitric oxide.*

$$\begin{aligned} & 2HNO_3 &&= H_2O &&+ 2NO &&+ 3O \\ 3Cu & + 3O &&= 3CuO && && \\ 3CuO & + 6HNO_3 &&= 3Cu(NO_3)_2 &&+ 3H_2O && \\ \hline 3\overset{0}{Cu} & + 8H\overset{+5}{N}O_3 &&= 3\overset{+2}{Cu}(NO_3)_2 &&+ 2\overset{+2}{N}O &&+ 4H_2O \end{aligned}$$

(c) *Cold and dilute nitric acid* oxidises copper to *cupric nitrate,* itself being reduced to *nitrous oxide.*

$$\begin{aligned} & 2HNO_3 &&= H_2O &&+ N_2O &&+ 4O \\ 4Cu & + 4O &&= 4CuO && && \\ 4CuO & + 8HNO_3 &&= 4Cu(NO_3)_2 &&+ 4H_2O && \\ \hline 4\overset{0}{Cu} & + 10H\overset{+5}{N}O_3 &&= 4\overset{+2}{Cu}(NO_3)_2 &&+ \overset{+1}{N}_2O &&+ 5H_2O \end{aligned}$$

(d) On passing *nitric acid vapours* over heated copper, it is oxidised by HNO_3 to give *black cupric* oxide and nitric acid is reduced to give *nitrogen.*

$$\begin{array}{l} 2HNO_3 = H_2O + N_2 + 5O \\ 5Cu + 5O \quad = 5CuO \\ \hline \overset{0}{5Cu} + 2H\overset{+5}{N}O_3 = 5\overset{+2}{Cu}O + \overset{0}{N_2} + H_2O \end{array}$$

(2) ***Aqua regia—Action of nitric acid on conc. HCl :***

When conc. HNO_3 is mixed with conc. HCl in the ratio 1 : 3 by volume, the latter is oxidised producing nascent chlorine, nitric acid being reduced to *nitrosyl chloride.*

$$3H\overset{-1}{Cl} + H\overset{+5}{N}O_3 = \overset{+1}{N}OCl + 2\overset{0}{Cl} + 2H_2O$$

This mixture of conc. HCl and conc. HNO_3 is called aqua regia. This is because of the fact that it can dissolve noble metals like gold, platinum. Which are not dissolved by any of these two acids acting alone. The liberated nascent chlorine attacks these noble metals to form their chloro compounds.

$$\begin{aligned} 3HCl + HNO_3 &= 2Cl + NOCl + 2H_2O \\ 2Au + 6Cl + 2HCl &= \underset{\text{Chloro auric acid}}{2HAuCl_4} \\ Pt + 2HCl + 4Cl &= \underset{\text{Chloro platinic acid}}{H_2(PtCl_6)} \end{aligned}$$

The *insoluble sulphides* of Hg, CO, Ni etc. are dissolved in aqua regia.

(3) ***Nitrating property of nitric acid :***

Organic compounds like *alcohols, sugar, terpentine* etc. are oxidised by conc. HNO_3. These substances burst into flames when nitric acid is added to these substances.

Nitric acid has *nitrating property.* In its reactions with many organic compounds one or more hydrogen atoms of the molecule of the organic compounds are substituted by nitro (NO_2) groups.

Thus *benzene* reacts with conc. HNO_3 in presence of conc. H_2SO_4 to produce *nitro benzene.* It oxidises cane suger to *oxalic* acid.

$$C_6H_6 + HNO_3 \xrightarrow[\text{conc. } H_2SO_4]{} C_6H_5NO_2 + H_2O$$

• Tests of nitric acid :

Nitric acid and nitrates are identified by the following tests—

(i) Copper turnings on being heated with conc. HNO_3 evolves brown fumes of nitrogen di-oxide.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

When a nitrate salt is heated with conc. H_2SO_4 and copper turnings, brown fumes of nitrogen di-oxide are evolved.

$$\begin{aligned} (KNO_3 + H_2SO_4 &= KHSO_4 + HNO_3) \times 4 \\ Cu + 4HNO_3 &= Cu(NO_3)_2 + 2NO_2 + 2H_2O \end{aligned}$$

(ii) Concentrated solution of a nitrate on being heated with *powdered aluminium* or *zinc* and *conc. NaOH* solution *liberates ammonia* which can be identified by its formation of white fumes in contact with conc. HCl.

$$4Zn + 7NaOH + NaNO_3 = 4Na_2ZnO_2 + NH_3 + 2H_2O$$
$$8Al + 5NaOH + 3NaNO_3 + 2H_2O = 8NaAlO_2 + 3NH_3$$

(iii) **Ring test :** This is the most popular and delicate test for detecting *nitric acid* and *nitrates.*

Equal volumes of nitric acid or an aqueous solution of a nitrate and freshly prepared ferrous sulphate solution are taken in a test tube and mixed together. After cooling the mixture, concentrated sulphuric acid is poured slowly down the side of the test tube without disturbing the mixture. Conc. H_2SO_4 being heavier liquid, collects at the bottom of the test tube with the layer of the mixture above it. A brown ring is found to be formed at the junction of the two liquids.

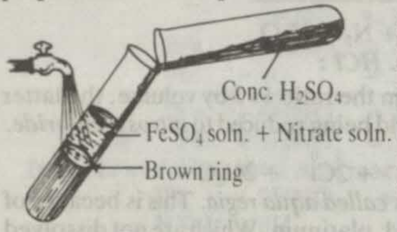


Fig. 2.20 : Ring test

Reactions involved : In this test the free nitric acid or the nitric acid, produced by the action of nitrate salt and conc. H_2SO_4, oxidises ferrous sulphate to ferric sulphate, itself being reduced to nitric oxide. The nitric oxide thus produced, combines with the rest of ferrous sulphate forming an additive compound of the composition $[Fe,(NO),(H_2O)_5]\ SO_4$. The brown ring is formed due to the formation of this compound.

$$\begin{aligned} NaNO_3 + H_2SO_4 &= NaHSO_4 + HNO_3 \\ 6FeSO_4 + 3H_2SO_4 + 2HNO_3 &= 3Fe_2(SO_4)_3 + 2NO + 4H_2O \\ FeSO_4 + 6H_2O &= [Fe(H_2O)_6]SO_4 \\ [Fe(H_2O)_6]SO_4 + NO &= \underset{\text{brown ring}}{[Fe(NO)\ (H_2O)_5]SO_4} + H_2O \end{aligned}$$

Infra-red studies confirm that NO is present as NO^+ state not as neutral NO. Magnetic moment (3.89 B.M) confirms the presence of 3 unpaired electrons so that Fe is in + 1 oxidation state. Thus the correct formula of the brown additive compound is $[\overset{I}{Fe}\ (H_2O)_5\ \overset{+}{N}O]SO_4$

$Pb(NO_3)_2$ is soluble in water, but while ring test is performed with $Pb(NO_3)_2$, on addition of $FeSO_4$ and H_2SO_4 to an aqueous solution of $Pb(NO_3)_2$, a curdy white precipitate of $PbSO_4$ appears. As a result, ring test for $Pb(NO_3)_2$ is not possible. This difficulty may be overcome by adding excess of H_2SO_4 to the aqueous solution of $Pb(NO_3)_2$ for complete precipitation of $PbSO_4$ and the precipitate is filtered off. With the filtrate ring test is performed when a brown ring is formed at the junction of two liquids.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4\downarrow + 2HNO_3$$
$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$
$$FeSO_4 + 5H_2O + NO = Fe[(NO)(H_2O)_5]SO_4$$

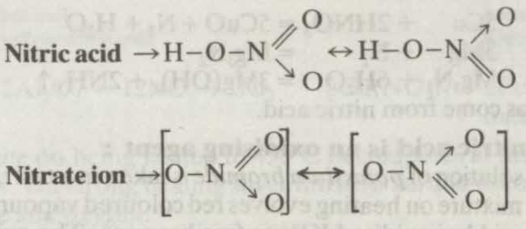
(iv) **Brucine test :** When nitric acid or a nitrate is added to a solution of brucine taken in a porcelain basin and pure sulphuric acid is added to it, a beautiful red colour is formed which proves the presence of nitric acid or nitrate radical.

- **Uses of nitric acid :**

In addition to its use in the laboratory as an *oxidant* and *nitrating* agent, it is used—(i) in the preparation of *explosives* such as *dynamite, gun cotton, nitro-glycerine, tri-nitro toluene* and *ammonium nitrate,* (ii) in the manufacture of *nitrate salts, fertilizers* and *sulphuric acid,* (iii) in the manufacture of *celluloid, collodion, cellophane, rayon* and *nitro cellulose* products, (iv) in the separation of gold from silver, in *etching designs on brass* and *bronze* vessels, (v) in the preparation of *aqua regia.*

- **Structure of nitric acid :**

Nitric acid and nitrate ion have triangular structure. The structure of HNO_3 can be explained by assuming that it is a resonance hybrid of following two structures.



• Prove that nitric acid contains nitrogen, hydrogen and oxygen :

(i) Concentrated nitric acid is allowed to drop on red hot pumic stone taken in a distilling flask. Nitric acid is thus thermally decomposed to produce a gas mixture which is allowed to pass successively through two U-tubes, the first one being kept on ice and the second one in a freezing mixture. A delivery tube is connected to the other end of the second U-tube.

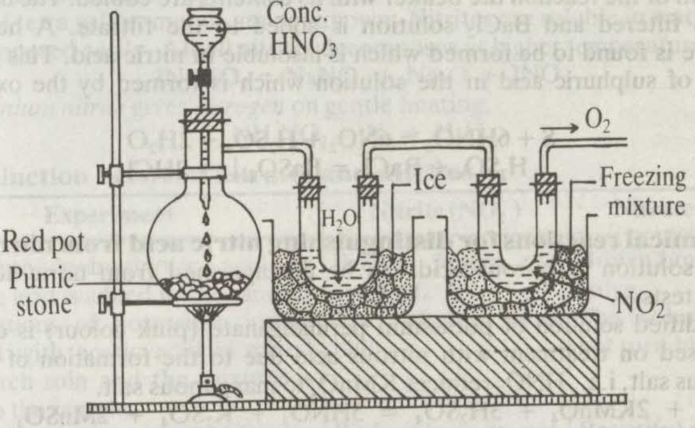


Fig 2.21 :

(ii) *Presence of oxygen :* A colourless gas is found to come out through the delivery tube which is collected in a gas jar. A glowing chip of wood bursts into flames when comes in contact with this gas. The gas is found to be absorbed in a alkaline pyrogallate solution turning it brown. Thus it is proved that the colourless gas is oxygen and it has come from nitric acid.

(iii) *Presence of hydrogen :* A colourless liquid is found to be collected in the first U-tube. This liquid when brought in contact with anhydrous copper sulphate (white) turns blue. This proves that the colourless liquid is nothing but water. Water contains hydrogen and this hydrogen has come from nitric acid.

$$4HNO_3 = 2H_2O + 4NO_2 + O_2$$

(iv) *Presence of nitrogen :* Nitric acid vapour is passed through a combustion tube containing red hot copper filings. The gas coming out of the combustion tube is collected and a burning magnesium ribbon is introduced in it. The magnesium ribbon continues to burn in it. After the completion of the reaction a greyish white residue is obtained which being treated with boiling water, gives off ammonia. This proves that the issuing gas from the combustion tube is nitrogen which reacts with burning magnesium to form magnesium nitride and this gives off ammonia on hydrolysis.

$$5Cu + 2HNO_3 = 5CuO + N_2 + H_2O$$
$$3Mg + N_2 = Mg_3N_2$$
$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3\uparrow$$

This nitrogen has come from nitric acid.

- **Prove that nitric acid is an oxidising agent :**

(i) A colourless solution of *potassium bromide* is taken in a test tube and nitric acid is added to it. The mixture on heating evolves red coloured vapours of bromine. This proves that nitric acid has oxidised KBr to free bromine. The oxidation number of bromine atom in KBr is −1 and that of free bromine is 0. As the oxidation number of bromine has been increased, so it is proved that KBr is oxidised to bromine by HNO_3.

$$6K\overset{-1}{Br} + 8HNO_3 = 6KNO_3 + 3\overset{0}{Br_2} + 2NO + 4H_2O$$

(ii) A small quantity of sulphur is taken in a beaker and conc. nitric acid is added to it. The beaker is then heated gently when brown fumes are liberated. After the completion of the reaction the beaker with its contents are cooled. The liquid in the beaker is filtered and $BaCl_2$ solution is added to the filtrate. A heavy white precipitate is found to be formed which is insoluble in nitric acid. This proves the presence of sulphuric acid in the solution which is formed by the oxidation of sulphur.

$$S + 6HNO_3 = 6NO_2 + H_2SO_4 + 2H_2O$$
$$H_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2HCl$$

- **Chemical reactions for distinguishing nitric acid from nitrous acid :**

Dilute solution of nitrous acid can be distinguished from nitric acid by the following tests—

(i) Acidified solution of potassium permanganate (pink colour) is completely decolourised on treatment with nitrous acid due to the formation of colourless manganous salt, i.e., HNO_2 reduces $KMnO_4$ to manganous salt.

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

Dilute nitric acid cannot decolourise the acidified $KMnO_4$ solution as HNO_3 has no reducing property.

(ii) When nitrous acid is added to a solution of brucine in pure H_2SO_4, it does not turn red. But when nitric acid is added to a mixture of brucine solution and pure sulphuric acid, a beautiful red colour is obtained.

[I] Nitrates : Salts of nitric acid are known as nitrates.

Preparation : The nitrates are prepared by the action of nitric acid on metals, metallic hydroxides or carbonates.

Excepting the basic nitrates of Pb and Bi, *all other metallic nitrates are soluble in water. Metallic nitrates decompose on strong heating.*

- **Action of heat on metallic nitrates.**

(i) *Nitrates of alkali metals e.g., sodium, potassium* on being strongly heated decompose to give *metallic nitrites* with the evolution of *oxygen.*

$$2NaNO_3 = 2NaNO_2 + O_2 \qquad 2KNO_3 = 2KNO_2 + O_2$$

(ii) *Nitrates of heavy metals (lead, copper, aluminium, mercury, iron, calcium* etc.) on strong heating decompose to produce their respective *oxides* liberating *oxygen* and brown fumes of *nitrogen di-oxide.*

$$2Pb(NO_3)_2 = \underset{\substack{\text{brown when}\\ \text{hot and}\\ \text{yellow when cold}}}{2PbO} + 4NO_2 + O_2, \qquad 2Zn(NO_3)_2 = \underset{\substack{\text{yellow when}\\ \text{hot and}\\ \text{white when cold}}}{2ZnO} + 4NO_2 + O_2$$

$$4Al(NO_3)_3 = 2Al_2O_3 + 12NO_2 + 3O_2 \qquad 2Cu(NO_3)_2 = \underset{\text{black}}{2CuO} + 4NO_2 + O_2$$

(iii) *Silver nitrate* on being heated to 450°C decomposes at first to produce *silver nitrite* and *oxygen*. On strong heating silver nitrite is further decomposed to *metallic silver, nitric oxide* and *oxygen*.

$$2AgNO_3 = 2AgNO_2 + O_2\uparrow \qquad 2AgNO_2 = 2Ag + 2NO + O_2\uparrow$$

(iv) *Ammonium nitrate* on gentle heating gives *nitrous oxide* and water.

$$NH_4NO_3 = N_2O + 2H_2O$$

[II] Nitrites : Nitrites are the salts of nitrous acid. As nitrous acid is a weak acid, it forms stable nitrite salts with strong bases.

$$HNO_2 + NaOH = NaNO_2 + H_2O$$

Thus nitrites of alkali metals, alkaline earth metals and silver are available, but excepting alkaline earth metals very few nitrites of divalent metals are known. Nitrites of tetra valent metals are not known. Nitrites are soluble in water. Nitrites are decomposed easily. Alkali nitrites decomposes at higher temperature.

$$3NaNO_2 = NaNO_3 + Na_2O + 2NO$$

Ammonium nitrite gives *nitrogen* on gentle heating.

$$NH_4NO_2 = N_2 + H_2O$$

- **Distinction between nitrates and nitrites :**

Experiment	Nitrite (NO_2)	Nitrate (NO_3)
(1) Dilute hydrochloric acid or sulphuric acid is added to the sample.	Brown fumes are evolved.	Brown fumes do not volve.
(2) Solutions of potassium iodide acidified with acetic acid is mixed with starch soln and the mixture is added to the sample.	The solution turns blue.	The solution does not turn blue.
(3) Brucine and conc. H_2SO_4 are added to the sample.	Red colour is not produced.	Beautiful red colour is produced.
(4) Solution of $KMnO_4$ acidified with H_2SO_4 is added to the sample.	The pink colour of $KMnO_4$ solution is discharged.	The pink colour of the $KMnO_4$ solution. is not discolourised.
(5) The sample is heated with urea and dil. H_2SO_4.	Colourless and odourless N_2 gas is evolved.	Nitrogen is not evolved.
(6) Ring test is performed with the the sample.	The whole of the solution turns brown	Brown ring is formed at the junction of acid and salt soln.

2.23. Large scale preparation of nitric acid.

On large scale, nitric acid is prepared by three methods—

(i) *By the catalytic oxidation of ammonia— Ostwald Process.*

(ii) *By direct combination of nitrogen and oxygen of air—Birkland and Eyde process.*

(iii) *By distillation of chili saltpetre with conc. H_2SO_4.*

[1] Ostwald process—by the catalytic oxidation of ammonia :

[A] **Raw materials used**—(i) *Ammonia* (ii) *Air.*

[B] **Principle :** (i) A mixture of *ammonia* (obtained by Haber's Process) and *excess air* is passed over *platinum gauze* heated to 750°C when ammonia is catalytically oxidised by the oxygen of air to produce *nitric oxide.*

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O + \text{Heat.}$$

(ii) The nitric oxide thus produced is further oxidised by the atmospheric oxygen to form nitrogen di-oxide.

$$2NO + O_2 = 2NO_2$$

(iii) Nitrogen di-oxide on being treated with hot water yields nitric acid and nitric oxide.

$$3NO_2 + H_2O = 2HNO_3 + NO\uparrow$$

[C] **Physico chemical conditions of the process to have a good yield :**

The main reaction of this process is the oxidation of ammonia to nitric oxide by the oxygen of air.

$$4NH_3 + 5O_2\,(\text{air}) \rightleftharpoons 4NO + 6H_2O + \text{Heat}$$

(i) It appears from the equation that the reaction is (a) reversible, (b) the forward reaction is exothermic and (c) the formation of nitric oxide by the oxidation of ammonia is accompanied by a little increase in volume.

(ii) ***The effect of temperature :***

As the forward reaction is exothermic, the reverse reaction is obviously endothermic. So according to Le Chatelier's principle the increase of temperature will favour the backward reaction resulting the poor yield of nitric oxide.

If the reaction is carried out at low temperature the reaction will proceed in a direction where the loss of heat is recovered. As the forward reaction is exothermic, the lowering of temperature will favour the forward reaction with a result of better yield. But the lowering of temperature decreases the rate of reaction to a great extent. Consequently it takes a longer period to attain the equilibrium. As much time cannot be allowed in a commercial process, a temperature has been selected at which the reaction proceeds at a fairly good speed giving a satisfactory yield of nitric oxide. The selected temperature is 750°C and the reaction is carried out at this temperature. This is called the *optimum temperature.*

(iii) ***The effect of pressure :***

As the forward reaction is accompanied by an increase in volume, there is an increase in pressure in the forward reaction. Consequently if the pressure is increased, the system will try to get rid of the extra pressure by proceeding the reaction in the reverse direction with a result of poor yield. So 7—8 atmosphere pressure is applied in this reaction to have a better yield.

(iv) ***Effect of catalyst :***

With a view to increasing the rate of reaction and to reach the equilibrium quickly *platinum wire gauze* is used as catalyst in this reaction.

(v) To stop the decomposition of the produced nitric oxide, the heated gas mixture $[NH_3+O_2\,(\text{air})]$ is very rapidly passed over the catalyst. The contact period between the gas mixture and the catalyst is about *one thousandth* part of a second, because the longer contact will decompose the produced nitric oxide to nitrogen and oxygen.

$$4NH_3 + 6NO = 5N_2 + 6H_2O. \qquad 4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

(vi) The gas mixture must be pure and dust free. The presence of any impurity will poison the valuable catalyst.

(vii) ***Proportion of the gas mixture :***

If the concentration of any one of the reactants is increased the forward reaction will be favoured resulting the greater yield of nitric oxide. Consequently a mixture of ammonia and air in the proportion of 1:7·5 by volume is used for the reaction.

[D] Procedure :

(i) In this process dry and pure ammonia and preheated dry air are mixed in the ratio 1:7·5 by volume. (ii) The gas mixture is first passed through a dust chamber to make it dust free. (iii) After this the gas mixture is admitted into an aluminium box called converter. Several screens of platinum wire gauze (catalyst) are stretched across the aluminium box. (iv) The catalyst is heated electrically to 750°C at the start of the reaction. The gas mixture is passed through the catalyst rapidly. (v) Once the reaction starts the heat produced by the exothermic reaction maintains the temperature of the catalyst. (vi) The gas mixture coming out of the converter contains nitric oxide, some nitrogen, excess of air and steam. (vii) The hot gas mixture is then cooled to 50°C by passing it through a heat exchanger where it transfers its heat to the fresh incoming mixture of ammonia and air. (viii) It is then led into an empty aluminium cylinder called oxidation chamber, where air is mixed with it. The nitric oxide is oxidised by the oxygen of air to nitrogen di-oxide. (ix) The nitrogen dioxide is then passed through a tower packed with quartz over which water flows from above. Nitrogen di-oxide is absorbed in water to form nitric acid solution (50%) which is collected from the bottom of the tower.

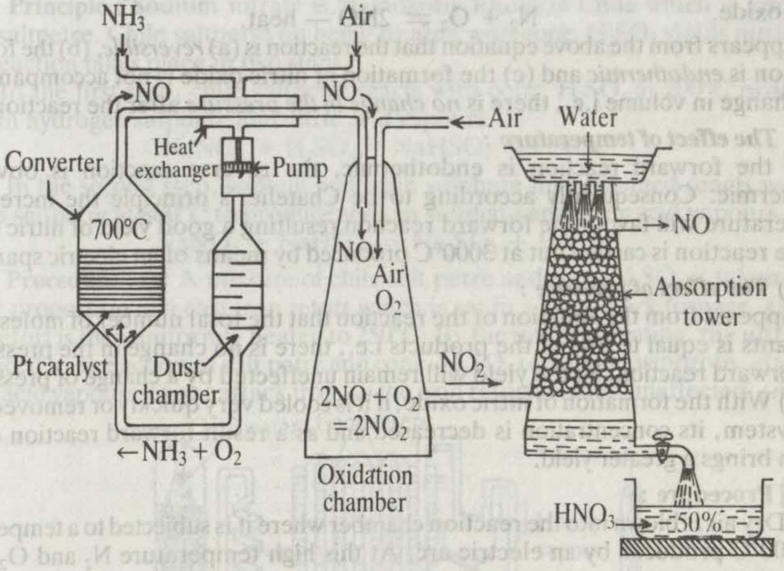


Fig 2.22 : Ostwald process of manufacturing of nitric acid

Concentration : The acid thus obtained is 50%. Concentrated nitric acid is obtained by heating this dilute acid to 120°C. The concentrated acid thus obtained on being distilled with conc. H_2SO_4 under reduced pressure yields 98% nitric acid.

[2] Birkeland and Eyde process or Arc process :

[A] Raw materials : Nitrogen and oxygen of the atmosphere.

[B] **Principle :** (i) In this process nitrogen of the atmosphere directly combines with the oxygen of air to produce nitric oxide.

$$N_2 + O_2 \rightleftharpoons 2NO - \text{heat}$$

(ii) The nitric oxide thus obtained in made to react with more oxygen of air to produce nitrogen di-oxide.

$$2NO + O_2 = 2NO_2$$

(iii) The produced nitrogen di-oxide on being treated with hot water yields nitric acid.

$$3NO_2 + H_2O = 2HNO_3 + NO$$

[C] **Physico chemical conditions of the process to have a good yield :**

(i) The main reaction of this process is the oxidation of atmospheric nitrogen to nitric oxide.

$$N_2 + O_2 \rightleftharpoons 2NO - \text{heat.}$$

It appears from the above equation that the reaction is (a) *reversible,* (b) the forward reaction is *endothermic* and (c) the formation of nitric oxide is not accompanied by any change in volume i.e., there is *no change in the pressure* after the reaction.

(ii) ***The effect of temperature :***

As the forward reaction is endothermic, the reverse reaction is obviously exothermic. Consequently according to Le Chatelier's principle the increase of temperature will favour the forward reaction resulting a good yield of nitric oxide. So the reaction is carried out at 3000°C produced by means of an electric spark.

(iii) ***The effect of pressure :***

It appears from the equation of the reaction that the total number of moles of the reactants is equal to that of the products i.e., there is no change in the pressure in the forward reaction. So the yield will remain uneffected by a change of pressure.

(iv) With the formation of nitric oxide, if it is cooled very quickly or removed from the system, its concentration is decreased and as a result forward reaction occurs which brings a greater yield.

[D] **Procedure :**

(i) Dry air is blown into the reaction chamber where it is subjected to a temperature of 3000°C produced by an electric arc. At this high temperature N_2 and O_2 of air combine together to form nitric oxide. (ii) To avoid the reverse reaction, the products are removed from the reaction chamber very quickly and is suddenly cooled down

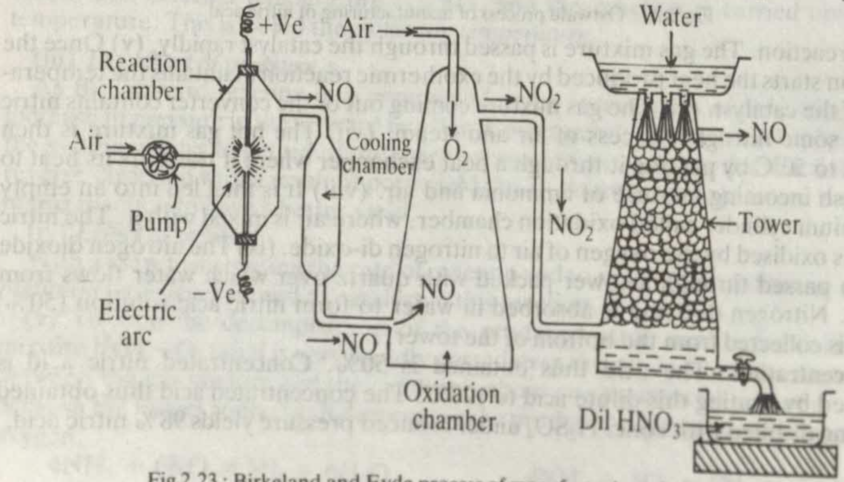


Fig 2.23 : Birkeland and Eyde process of manufacturing of nitric acid

to 1000°C. (iii) The cooled nitric oxide along with air is led to oxidation chamber where additional air is mixed. Here nitric oxide is oxidised by the oxygen of air to produce nitrogen di-oxide. (iv) The NO_2 is then passed up a tower packed with quartz stones. NO_2 is absorbed by the shower of water coming down the tower. (v) NO_2 on being absorbed in water yields 50% nitric acid solution, which is collected from the bottom of the tower.

This process is very costly due to the high consumption of electric energy in order to produce high temperature.

[3] **By the distillation of Chile saltpetre with conc. H_2SO_4.**

[A] **Raw materials :** (i) Chile saltpetre ($NaNO_3$), (ii) concentrated sulphuric acid.

[B] **Principle :** Sodium nitrate is abundantly found in Chile which is known as chile saltpetre. Chile saltpetre on being treated with conc. H_2SO_4 yields nitric acid. The reaction takes place in two steps.

(i) In the first step, chile saltpetre reacts with conc. H_2SO_4 at 200°C producing sodium hydrogen sulphate and nitric acid vapours.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3\uparrow$$

(ii) In the second step, sodium hydrogen sulphate thus obtained reacts with the excess saltpetre at 800°C to produce sodium sulphate and nitric acid vapours.

$$NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3\uparrow$$

[C] **Procedure :** (i) A mixture of chile salt petre and conc. H_2SO_4 is taken in 3:2 molar proportion in a cast iron retort which is set in a brick work furnace. (ii) The iron retort is then uniformly heated to 250°C. By the uniform heating, the nitric acid produced by the action of salt petre and conc. H_2SO_4 remains in vaporous state. As nitric acid vapours do not attack iron, so the iron retort remains uneffected. (iii) The HNO_3 vapours thus produced come out of the retort and pass through a series of water-cooled condensing pipes which are acid resistant. The nitric acid vapours while passing through these pipes get condensed and collect in the stoneware receiver as concentrated acid.

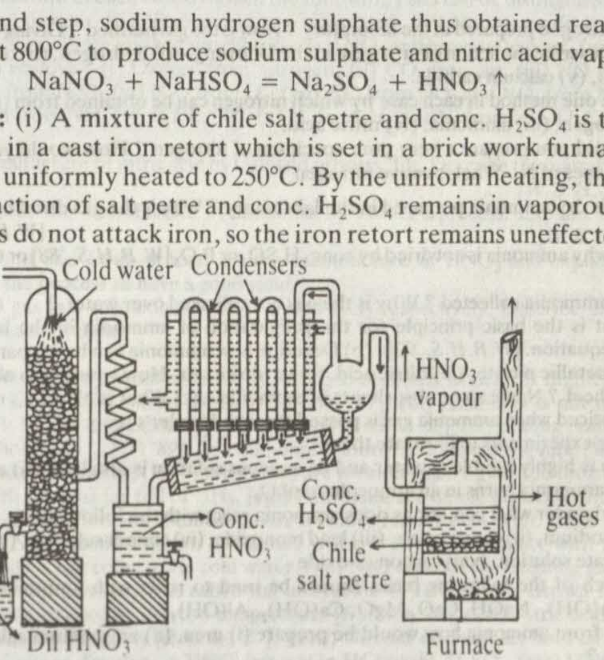


Fig 2.24 : Manufacturing of nitric acid from chile saltpetre

(iv) The uncondensed vapours, which contains mainly NO_2, produced by the thermal decomposition of HNO_3 are made to pass through a scrubber packed with quartz, from the top of which stream of water is allowed to trickle down. In this scrubber HNO_3 vapours and NO_2 are absorbed by the shower of water coming down forming dilute nitric acid. This dilute nitric acid is collected from the bottom of the scrubber.

The residue left in the iron retort is known as *nitre cake* and is used in dying and bleaching industry.

• Exercises •

1. Show with proper reasonings that air is a mixture and not a chemical compound. *[H.S. 1986, '88, (Trip). '81]*

2. 'Air is a mixture and not a chemical compound'—how would you prove it ? *[H.S. (Trip). '74]*

3. How would you prove that air and water contain a common constituent ? What are the evidences to indicate that in one case, the common constituent is chemically combined and in other it is merely form a part of the mixture. *[W.B.J.E.E. '78]*

4. Describe the experiment in which Lavoisier proved that air is a mixture. *[H.S. '72]*

5. Write down the names of the constituents of air and give the approximate quantity. Prove experimentally the presence of O_2, N_2, CO_2 in air. Name the inert gases present in air. *[H.S. (Trip) '83]*

6. How would you prove that air and ammonia contain a common constituent ? What are the evidences to indicate that in ammonia the common constituent is chemically combined and in air it is only a part of mixture ?

7. Explain what is meant by nitrogen cycle in nature ? *[W.B.H.S. '89]*

8. What is meant by fixation of nitrogen ? State some methods for the artificial fixation of atmospheric nitrogen.

9. How is nitrogen prepared in the laboratory ? How is the gas purified ? Giving conditions of reactions and equation, describe the action of nitrogen on the following—(i) hydrogen, (ii) oxygen, (iii) aluminium, (iv) magnesium, (v) calcium carbide.

10. Describe one method in each case by which nitrogen can be obtained from (i) air, (ii) a compound containing nitrogen, (iii) ammonia, (iv) nitric acid.

11. How would you prepare a very pure specimen of nitrogen ? How would you identify nitrogen ? Mention some uses of N_2. What is active nitrogen ?

12. (i) How is dry ammonia prepared in the laboratory ? Why is the gas dried by quick lime ? *[W.B.H.S. '78, J.E.E. '90]*

(ii) Explain why ammonia is not dried by conc. H_2SO_4 or P_2O_5 *[W.B.H.S. '88]* or $CaCl_2$ *[W.B.H.S. '88]*

(iii) How is ammonia collected ? Why is the gas not collected over water ?

13. (a) What is the basic principle for the preparation of ammonia in the laboratory ? Give one example with equation. *[W.B.H.S. '92]* (b) Describe how ammonia can be prepared from—(i) a metallic nitride, (ii) a metallic nitrate, (iii) nitric acid, (iv) a nitrite salt. How would you obtain NH_3 without the application of heat ? Name some absorbants of ammonia. (c) What is Nessler's reagent ? What visible changes are noticed when ammonia gas is passed through Nessler's reagent ? *[W.B.H.S. '92]*

14. Describe experiments to illustrate that—

(i) ammonia is highly soluble in water and its aqueous solution is alkaline, (ii) ammonia has reducing property, (iii) ammonia burns in an atmosphere of O_2.

15. How and under what conditions does ammonia react with the following—

(i) metallic sodium, (ii) cupric oxide, (iii) lead monoxide, (iv) copper sulphate, (v) oxygen, (vi) chlorine, (vii) silver nitrate solution. (viii) carbon di-oxide.

16. (a) Which of the following bases should be used to react with ammonium chloride to obtain ammonia ? $Cu(OH)_2$, $NaOH$, CaO, MgO, $Ca(OH)_2$, $Al(OH)_3$.

(b) Starting from ammonia how would be prepare (i) urea, (ii) ammonium sulphate, (iii) HNO_3 and (iv) Hydrogen ?

(c) Write two resonance structures of N_2O that satisfy the octet rule.

(d) Give the structural formula of NO and N_2O_5. *[I.I.T. '90]*

17. How would you prove the presence of N_2 and H_2 in ammonia ?

18. (a) Write down the names of the oxides of nitrogen with their formulae. What is laughing gas ?

(b) How is nitrous oxide prepared in the laboratory ? Give a neat sketch of the apparatus used.

(c) Compare the properties of different oxides of nitrogen. *[H.S. (Trip.) '80]*

19. (a) Describe how the nitrous oxide obtained in the laboratory is purified, (b) How would you distinguish between (i) nitrous oxide and oxygen. (ii) NO and N_2O. *[W.B.H.S. '92]* (c) Prove that nitrous oxide contains nitrogen.

20. How is nitric oxide prepared in the laboratory ? How is the gas purified and collected ? Prove that nitric oxide contains nitrogen.

21. How could you obtain a pure sample of nitrogen di-oxide in the laboratory ? What is its relation with N_2O_4 ? Give a comparative account of the properties of N_2O, NO and NO_2.

22. Describe how would you obtain an aqueous solution of nitrous acid in the laboratory. Why the solution of HNO_2 cannnot be concentrated ? Illustrate the oxidising and reducing action of nitrous acid. Mention one test to identify nitrous acid.

23. (a) How is nitric acid prepared in the laboratory ? Mention its uses. What is fuming nitric acid ? (b) Compare the properties of nitric acid and nitrous acid when they are treated separately with (i) acidified $KMnO_4$ solution. (ii) KBr (iii) acidified $FeSO_4$ solution.

24. Prove that (i) nitric acid is an oxidising agent [*W.B.H.S. '93*] (ii) nitric acid contains nitrogen, hydrogen and oxygen. [*W.B.H.S. '86, J.E.E. '87*]

25. Starting from nitric acid how would you obtain—

(i) ammonia, (ii) nitrogen, (iii) hydrogen, (iv) nitrous acid, (v) NO_2 and N_2O_5.

26. Mention some tests to identify nitrates and nitric acid. What difficulty will you encounter in the ring test of nitrate with lead nitrate ? How will you overcome the difficulty ? [*J.E.E. '93*] What is *aqua regia* ? Why is it so called ?

27. How would you obtain—

(i) Nitrogen, nitric oxide and nitrous oxide from nitric acid [*W.B.J.E. '88*], (ii) Ammonia from nitrogen and vice versa, (iii) Ammonia from nitric acid and vice-versa [*W.B.H.S. '82*], (iv) Nitrogen from a nitrate and a nitrite [*W.B.H.S. '90*], (v) Ammonia from urea [*W.B.H.S. '86, J.E.E. '88*], (vi) Hydrogen from nitric acid [*W.B.H.S. '88*], (vii) Nitrous acid from nitric acid and vice versa, (viii) Urea from ammonia [*W.B.H.S. '84*], (ix) N_2 from $Pb(NO_3)_2$ [*J.E.E. '93*]

28. State chemical reaction in each case by which the following pairs can be distinguished—

(i) Nitrous oxide and oxygen, (ii) Nitrous acid and nitric acid, (iii) Nitrous oxide and nitric oxide, [*W.B.H.S. '92*] (iv) Sodium nitrate and sodium chloride, (vi) NO_2 and bromine vapour, (vii) N_2 and O_2.

29. How would you remove—(i) Oxygen from nitrogen, (ii) CO_2 from air, (iii) NO from N_2O, (iv) N_2O from NO, (v) O_2 from N_2O, (vi) N_2O from O_2, (vii) NO from NO_2 and NO_2 from NO, (viii) NO_2 from HNO_3, (ix) Water from NH_3 [*W.B.J.E. '88*], (x) N_2 from H_2, (xi)N_2 from NH_3 [*J.E.E. '93*] [*W.B.H.S. '89*]

30. Describe the manufacture of nitric acid by Ostwald process. Or, Describe the manufacture of nitric acid from ammonia. [*W.B.H.S. '87, '91, '93*]

31. Give an account of the manufacture of ammonia by Haber's process. Explain the theoretical principle involved. [*W.B.J.E.E. '88, '93*]

32. Describe Birkeland and Eyde process for the manufacture of HNO_3 and explain the physico chemical conditions of the process to have a good yield.

33. You are given 3 gas jars containing N_2O, NO and NO_2 respectively. Describe experiments by which you can identify each of them.

34. Explain why—

(i) Nitrogen is inert at ordinary temperature, (ii) Nitrogen obtained from air is slightly heavier than that of prepared from ammonium nitrite [*W.B.J.E.E. '83, '87*], (iii) Ammonia is not dried by conc. H_2SO_4 or P_2O_5 or $CaCl_2$ but it can be dried by quicklime [*W.B.H.S. '88*], (iv) Boiling point of ammonia is higher than that of phosphine [*I.I.T. '89*], (v) Ammonia is more basic than phosphine [*W.B.H.S. '91*], (vi) Ammonia has reducing property, (vii) White fumes are formed when a glass rod moisted with conc. HCl is held at the mouth of a gas jar full of NH_3, (viii) Ammonia is a dipole molecule [*I.S.C. '87*], (ix) Nitrous oxide supports combustion and combustion occurs more readily than in air. [*W.B.H.S. '92*], (x) Colourless and neutral NO becomes brown and acidic when it comes in contact with air [*H.S. '80, W.B.J.E.E. '80*], (xi) N_2O is not collected in cold water, (xii) N_2O is called the laughing gas. (xiii) NO is a neutral oxide [*I.S.C. '89*], (xiv) N_2O_5 is called the anhydride of HNO_3, (xv) Brown fumes of NO_2 becomes almost colourless on cooling it to low temperature [*Roorke, '87*], (xvi) Nitric acid has oxidising property but has no reducing property [*Roorke, '87*], (xvii) Nitrous acid can act both as oxidising and reducing agent, (xviii) Copper dissolves in HNO_3 but not in HCl or dil. H_2SO_4, (xix) HNO_3 is not used in the preparation of H_2S [*W.B.H.S. '83, '93*], (xx) Conc. HCl is not used in the preparation of HNO_3 from KNO_3 [*W.B.H.S. '85*], (xxi) During the preparation of HNO_3 by the action of conc. H_2SO_4 on $NaNO_3$, the temperature is not allowed to increase above 200°C, (xxii) Gold dissolves in *aqua regia* [*Roorke, '88*], (xxiii) Most metal can not liberate H_2 from HNO_3 [*W.B.H.S. '88*] (xxiv) 'Tajmahal' is susceptible to atmospheric damage. [*W.B.H.S. '92*], (xxv) The colour of conc. HNO_3 is usually yellowish. [*W.B.H.S. '92, I.I.T. '80*], (xxvi) A bottle of liquor ammonia should be cooled before opening [*I.I.T. '83*], (xxvii) Ammonia is a good complexing agent, (xxviii) N_2 is a gas while the other members of the group are solids, (xxix) Burning Mg continues to burn in NO while burning S is extinguished, (xxx) KNO_3 is used in gun powder [*W.B.J.E.E. '93*]

35. State giving equations and mentioning any visual change what happens when—

(i) Ammonia is passed through silver nitrate solution [*W.B.H.S. '85*], (ii) Ammonia is passed separately through $FeCl_3$ and $AlCl_3$ solution [*W.B.H.S. '87*], (iii) Zinc powder is added to a mixture of (a) sodium nitrate and NaOH solution, (b) Sodium nitrite and NaOH solution and boiled [*W.B.H.S. '74,* *J.E. '82*], (iv) Excess ammonia is passed through copper sulphate solution, (v) Ammonia is passed separately over (a) heated sodium (b) heated copper oxide [*W.B.H.S. '83, J.E. '89*], (vi) A paste of bleaching powder is added to NH_4OH, (vii) The gas obtained by heating a mixture of ammonium sulphate and NaOH is passed over heated PbO, (viii) $AgNO_3$ is treated with NaCl solution and the product is treated with excess of NH_4OH, (x) A mixture of air and ammonia is passed over heated platinum gauze, (xi) Ammonia is treated with Nessler's reagent, (xii) N_2 is passed over heated CaC_2 and the product is treated with water [*W.B.H.S. '74, J.E. '88, '91*], (xiii) To a concentrated solution of NaOH, sodium nitrite and Al powder are added and boiled [*W.B.H.S. '85*], (xiv) A gas obtained by the action of 1 : 1 HNO_3 on copper is passed through $FeSO_4$ solution, (xv) Ammonium nitrite and lead nitrate are heated separately [*W.B.H.S. (T) '82*], (xvi) The gas obtained by heating ammonium nitrite is passed over heated magnesium and the product is treated with boiling water, (xvii) Iodine is boiled with conc. HNO_3 [*H.S. (T) '82*], (xviii) $Al(NO_3)_3$ is strongly heated [*W.B.H.S. '82*], (xix) P_2O_5 is heated with conc. HNO_3 [*W.B.H.S. '80*], (xx) Conc. H_2SO_4 is added to a mixture of the solution of $NaNO_3$ and $FeSO_4$ [*W.B.H.S. '86, J.E. '89*], (xxi) Iron is treated with cold HNO_3 [*HS (T) '81*], (xxii) Sulphur is boiled with conc. HNO_3 and the product is treated with $BaCl_2$ solution, (xxiii) Cu is treated with dil. HNO_3, (xxiv) A mixture of $NaNO_2$ and NH_4Cl is heated [*W.B.H.S. '91*], (xxv) The gas obtained by heating a mixture of KNO_3 and conc. H_2SO_4 is dissolved in water and H_2S is passed through the solution, (xxvi) N_2 is passed over heated calcium and the product is treated with boiling water, (xxvii) Ammonium dichromate and barium azide are heated separately [*J.E. '89*], (xxviii) A mixture of NO and Cl_2 is passed over heated charcoal, (xxix) HNO_3 vapour is passed over heated Cu and the gas obtained is passed over strongly heated CaC_2 [*H.S. '93*], (xxx) NO is passed through an acidified solution of $KMnO_4$, (xxxi) A burning piece of Na is introduced into a jar of N_2O, (xxxii) KI is added to a solution of $NaNO_2$ acidified with H_2SO_4 [*W.B.H.S. '86*], (xxxiii) Conc. HNO_3 is added dropwise on red hot pumic stone, (xxxiv) HNO_3 is reacted with (a) $FeSO_4$ (b) Mg [*W.B.H.S. '91*], (xxxv) Charcoal dust is heated with conc. HNO_3 [*W.B.H.S. '85*], (xxxvi) The product obtained by the reaction of Mg with N_2 is treated with HCl [*WBJE '89*], (xxxvii) Gold is treated with aqua regia [*I.I.T. '87*], (xxxviii) Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda [*I.I.T. '91*], (xxxix) Tin is boiled with conc. HNO_3 [*Roorkee '88*], (xl) Magnesium is boiled with very dilute HNO_3, (xli) Dilute nitric acid is slowly added to metallic tin [*I.I.T. '87*], (xlii) Mg is treated with very dilute HNO_3, (xliii) Dilute NH_4OH is added to a mixture of AgCl and mercurous chloride, (xliv) Aqueous ammonia is passed through $KMnO_4$ solution [*I.I.T. '91*].

36. A non combustible gas is passed over heated magnesium and the product obtained is treated with water when a new gas is obtained. This new gas on passing over heated CuO yields the original gas. Identify the original gas. Give the equations of the reactions involved. [*J.E.E. '90*]

37. A crystalline salt (A) responds to ring test. On heating (A) a colourless gas (B) is obtained which supports combustion of a glowing chip of wood but is not absorbed by alkaline pyrogallate solution. When (B) is passed over heated copper a colourless gas (C) is produced which is absorbed by burning Mg producing (D). When (D) is treated with boiling water yields ammonia. Identify (A), (B), (C) and (D). [***Ans.*** $A = NH_4NO_3$, $B = N_2O$, $C = N_2$, $D = Mg_3N_2$]

38. When a mixture of a sodium salt (A) and NH_4Cl solution is heated yields N_2O. On heating strongly (A) gives (B) and O_2. A mixture of (B) and NH_4Cl on gentle heating gives a colourless gas (C). On passing (C) over heated CaC_2 (D) is obtained which on treatment with steam yields a gas (E). Identify (A), (B), (C), (D) and (E) [***Ans.*** $A = NaNO_3$, $B = NaNO_2$, $C = N_2$, $D = CaCN_2$, $E = NH_3$]

39. Burning Mg is introduced into a jar of a colourless gas (A). The product obtained is treated with boiling water when another gas (B) having pungent odour is obtained. When (B) gas is passed over heated cupric oxide (A) gas is obtained. Identify (A) and (B). [***Ans.*** $A = N_2$, $B = NH_3$].

40. Nitrous acid is readily converted to nitric acid and nitric oxide. Express the reaction with chemical equation. Why is it called a disproportionation reaction ? Mention the oxidation number of nitrogen in nitrous acid, nitric acid and nitric oxide.

41. Objective type questions : Tick the correct answer—

(i) Laughing gas is (a) NO (b) NO_2 (c) N_2O. (ii) The stablest oxide of N_2 is (a) N_2O (b) NO (c) NO_2 (d) N_2O_5. (iii) Neutral oxide of N_2 is (a) NO_2 (b) N_2O (c) N_2O_5. (iv) A colourless gas when comes in contact with air turns brown, the gas may be (a) N_2O (b) NO_2 (c) NO. (v) NO is (a) reducing agent (b) oxidising agent (c) both an oxidising and a reducing agent (d) neither an oxidant nor a reductant. (vi) Nitrous acid forms (a) Nitrate (b) Nitrite (c) Nitride. (vii) Nitrogen of air is converted to nitric acid by (a) Haber's process (b) Ostwald's process (c) Contact process. (viii) Which of the following is both an oxidising and a reducing agent (a) N_2O (b) HNO_3 (c) HNO_2 (d) NO (e) NO_2. (ix) Which of the following metals is rendered passive by HNO_3 (a) Zn (b) Cu (c) Fe (d) Ag. (x) NO_2 can be prepared by heating (a) KNO_3 (b) NH_4NO_3 (c) $NaNO_3$ (d) $Pb(NO_3)_2$. (xi) Ring test matches with (a) chlorides, (b) sulphates, (c) nitrates, (d) sulphides, (xii) Nitric acid is (a) reducing agent (b) weak monobasic acid (c) oxidising agent (d) strong dibasic acid. (xiii) Aqua regia dissolves gold because it contains nascent (a) Cl (b) H (c) O (d) N. (xiv) Metal hydroxide which is soluble in ammonia (excess) is (a) $Fe(OH)_3$ (b) $Fe(OH)_2$ (c) $Al(OH)_3$

(d) $Cu(OH)_2$. (xv) Reddish brown coloured gas formed when NO is oxidised by air is (a) N_2O_3 (b) N_2O_4 (c) NO_2 (d) N_2O_3 [*I.I.T.* '79]. (xvi) Which of the following is coloured (a) NO(b) N_2O (c) N_2O_4 (d) NO_2 [*I.I.T.* '80]. (xvii) Which one of the following is strongest base ? (a) A_sH_3 (b) PH_3 (c) NH_3 [*I.I.T.* '89]. (xviii) Nitrogen (I) oxide is produced by the (a) Thermal decomposition of NH_4NO_3 (b) Disproportionation of N_2O_4 (c) thermal decomposition of NH_4NO_2 (d) action if hydroxyl amine with HNO_2 [*I.I.T.* '89] (xix) Ammonia can be dried by (a) Conc H_2SO_4 (b) P_2O_5 (c) $CaCl_2$ (d) $CuSO_4$ [*I.I.T.* '89]. (xx) NH_3 is dissolved fairly in (a) Hg_2Cl_2 (b) $PbCl_2$ (c) $Al(OH)_3$ (d) $Ca(OH)_2$ [*I.I.T.* '93].

42.. Fill in the blanks—

(i) The oxide of nitrogen which is absorbed in alcohol is ___. (ii) Nitric oxide is paramagnetic because it has ___ electron. (iii) ___ produces reddish brown fumes of ___ in air. (iv) Dehydration of HNO_3 yields ___. (v) Nitrolium is a mixture of ___ and ___. (vi) The oxide of nitrogen which is solid at room temperature is ___. In solid form it exists as ___. (vii) ___ and ___ are neutral oxides of N_2. (viii) Aqueous solution of ammonia contains ___, ___, ___ and ___. (ix) The acids obtained due to lightning discharge followed by rain are ___. (x) ___ is a mixed anhydride of HNO_2 and HNO_3. (xi) P reacts with HNO_3 to form ___, ___ and ___. (xii) P_2O_5 reacts with conc. HNO_3 to form ___ and ___.

43. (i) Write the two resonance structures of N_2O that satisfy the octet rule. [*I.I.T.* '90], (ii) Give the structural formula of nitric oxide, (iii) Give one example of each of the oxidation states of nitrogen (-3 to $+5$)

44. State whether the following statement is true or false ?

(i) NO is the anhydride of HNO_3, (ii) NO, though an odd electron molecule, is diamagnatic in liquid state. [*I.I.T.* '91], (iii) N_2O does not support combustion, (iv) NH_3 can be used as refrigerant, (v) NO is heavier than O_2.

45. (a) In which of the following reaction, ammonia and ammonium ion is acting as a reducing agent ?

(i) $3CuO + 2NH_3 = 3Cu + N_2 + 3H_2O$

(ii) $NH_4Cl + NaNO_3 = N_2 + NaCl + 2H_2O$

(iii) $NH_3 + HCl = NH_4Cl$

(b) Of the following, which one has three electron bond in its structure ?

(i) Nitrous oxide, (ii) Nitric oxide, (iii) Nitrogen di-oxide.

3

Boron and its compounds

• BORON •

Symbol—B. At wt. = 10·82 At No. = 5 Valency = 3
Electronic arrangement— $1s^2\,2s^2\,2p^1$ Position in Periodic table = III B.

The use of borax as a flux was well known from early ages, but it was isolated by **Davy** in 1807 by the electrolysis of moist boric acid. In 1808 Davy produced this element by heating fused boron trioxide with potassium.

It is a **metalloid** having two stable isotopes of mass number 10 and 11. It occurs in the allotropic forms—**crystalline boron** and **amorphous boron.**

3.1. Occurrence of Boron.

Boron does not occur in free state in nature. The minerals of boron are found in large quantities in volcanic regions and near the hot springs. The principal minerals are—

(1) **Borax ($Na_2B_4O_7$, $10H_2O$)**, (2) **Borocite ($2Mg_3B_8O_{11}$, $MgCl_2$)**, (3) **Colemanite ($Ca_2B_6O_{11}$, $5H_2O$)**, (4) **Pandaramite ($Ca_2B_6O_{11}$, $3H_2O$)**, (5) **Ulexite ($Na_2B_4O_7$, $Ca_2B_6O_{11}$), $16H_2O$)**, (6) **Kernite ($Na_2B_4O_7$, $4H_2O$)**, (7) **Boronatrocalcite (CaB_4O_7, $NaBO_2$, $8H_2O$).**

3.2. Preparation of Boron.

[A] Preparation of amorphous boron :

(1) **From boron tri-oxide :** Amorphous boron is prepared by reducing *boron tri-oxide* with *magnesium powder* or *metallic sodium* or *potassium.*

$$B_2O_3 + 3Mg = 3MgO + 2B$$
$$B_2O_3 + 6K = 3K_2O + 2B$$

Procedure : (i) An intimate mixture of powdered boron tri-oxide and magnesium powder is taken in a covered crucible made of silica. The mixture is strongly heated. (ii) The fused mass thus obtained is cooled and boiled with dilute hydrochloric acid to dissolve the unreacted magnesium, magnesium oxide and magnesium boride (Mg_3B_2) which may be produced in small quantity. (iii) The undissolved boron is separated from the solution by filtration. Boron is obtained as brown residue. (iv) It is washed well and finally dried in a steam oven. Boron thus obtained is about 93·8% pure.

Purification : The boron thus prepared is contaminated with silicon and silica. It is treated with hot hydrofluoric acid when silicon and silica are removed and boron of 98·3% purity is obtained.

(2) **From potassium borofluoride :**

Amorphous boron may also be prepared by heating *potassium boro fluoride* with *potassium* or *magnesium powder* in a covered crucible.

$$2KBF_4 + 3Mg = 2KF + 3MgF_2 + 2B$$
$$KBF_4 + 3K = 4KF + B$$

[B] Preparation of crystalline boron :

(i) Crystalline boron may be obtained by cooling **molten amorphous boron (m.p. 2300°C).**

(ii) Crystalline boron is prepared by subjecting a mixture of *boron tri-chloride* or *boron tri-bromide* vapours and *hydrogen* to electric spark between water cooled tungsten or copper electrodes. Boron tri-chloride or tri-bromide is reduced by hydrogen yielding pure crystalline boron.

$$2BCl_3 + 3H_2 = 2B + 6HCl.$$

(iii) Crystalline boron may also be obtained by the thermal decomposition of boron tri-chloride or bromide in contact with electrically heated tungsten filament at 1200°C.

[*Boron tri-oxide cannot be reduced by carbon even at white hot.*]

Crystalline boron can also be prepared by dissolving amorphous boron in molten aluminium at high temperature (2300°C). On cooling the resulting solution deposits crystals of boron which is boiled with NaOH solution to remove any aluminium present in it.

3.3. Properties of Boron.

[A] **Physical :** Boron is *hard steel* grey or a brown solid having density of 1·73 g/cc while crystalline boron is steel grey crystalline solid. Crystalline boron is very hard like diamond. Its density is 2·34 g/cc. Both the forms melt at 2300°C. It has metallic lustre. It is *non conductor of heat and electricity.*

[B] **Chemical :**

(a) **Crystalline boron :**

(i) Crystalline boron is very hard and chemically inert. It is not oxidised when heated strongly in air or oxygen.

(ii) It is not attacked by hot and concentrated nitric acid, sulphuric acid or hydrochloric acid or even by hydrofluoric acid.

(iii) It is oxidised to *borate* when fused with *sodium peroxide* or a mixture of *sodium carbonate* and *potassium nitrate.*

(b) **Amorphous boron :**

(i) Amorphous boron is comparatively more active than the crystalline form. At ordinary temperature amorphous boron is not attacked by air or oxygen but at 700°C it burns in air with a *reddish flame* producing *boron tri-oxide* and some *boron nitride.*

$$4B + 3O_2 = 2B_2O_3 \qquad 2B + N_2 = 2BN$$

(ii) **Action on nitrogen :** When boron is heated in a current of nitrogen, *boron nitride* is obtained. It is slippery and resembles graphite in its structure. That is why it is called *inorganic graphite.*

$$2B + N_2 = 2BN$$

Boron nitride on treatment with steam, is readily decomposed to give *ammonia* and *boric acid.*

$$BN + 3H.OH = NH_3 + H_3BO_3$$

(iii) **Action on alkalis :** It reacts with *fused alkalis* or their concentrated solutions producing *alkali metaborates* and evolving *hydrogen.*

$$2B + 2NaOH + 2H_2O = 2NaBO_2 + 3H_2$$

(iv) **Action on water :** Boron is unaffected by water at ordinary temperature, but is oxidised to boron tri-oxide by *super heated steam.*

$$2B + 3H.OH = B_2O_3 + 3H_2$$

(v) **Action on oxidising acids (conc. H_2SO_4, HNO_3) :**

Boron when treated with concentrated H_2SO_4 or nitric acid, is oxidised to boric acid. It is unaffected in hydrochloric acid.

$$\begin{array}{c}
(H_2SO_4 = H_2O + SO_2 + O) \times 3 \\
2B + 3O = B_2O_3 \\
B_2O_3 + 3H_2O = 2H_3BO_3 \\
\hline
3H_2SO_4 + 2\overset{0}{B} = 2H_3\overset{+3}{B}O_3 + 3SO_2
\end{array}$$

$$\begin{array}{c}
(2HNO_3 = H_2O + 2NO_2 + O) \times 3 \\
2B + 3O = B_2O_3 \\
B_2O_3 + 3H_2O = 2H_3BO_3 \\
\hline
6HNO_3 + 2B = 2H_3BO_3 + 6NO_2
\end{array}$$

(vi) **Action on metals :** In electric furnace at high temperature boron combines with most metals producing *metallic borides.*

$$3Mg + 2B = Mg_3B_2$$
$$3Ca + 2B = Ca_3B_2$$

Borides are hard and inert. They have high electrical conductivity than their corresponding metals.

(vi) **Action on halogen :** Boron *ingnites in fluorine* spontaneously producing *boron tri-fluoride.*

$$2B + 3F_2 = 2BF_3$$

At an elevated temperature it combines with chlorine producing *boron tri-chloride* which undergoes *hydrolysis* yielding *boric acid.*

$$2B + 3Cl_2 = 2BCl_3$$
$$BCl_3 + 3H.OH = H_3BO_3 + 3HCl$$

This is why boron halides have got acid property.

(viii) **Action on hydrogen :** Boron does not combine with hydrogen directly, but *boro ethane* or *diborane* (B_2H_6), *boro butane* (B_4H_{10}) are produced when magnesium boride is treated with dil. HCl at 50°C. These hydrides of boron on hydrolysis give *hydrogen* and *boric acid.*

$$Mg_3B_2 + 6HCl = 3MgCl_2 + B_2H_6$$
$$B_2H_6 + 6H.OH = 2H_3BO_3 + 6H_2$$

(ix) **Action on Carbon :** In electric furnace at high temperature boron combines with carbon forming *boron carbide.* Boron carbide (B_4C) is one of the hardest substance known. *It is next to diamond in hardness.*

$$4B + C = B_4C.$$

(x) **Reducing action of boron :** At high temperatures silica or CO_2 are reduced by boron.

$$3SiO_2 + 4B = 2B_2O_3 + 3Si$$
$$3CO_2 + 4B = 2B_2O_3 + 3C$$

- **Distinction between crystalline boron and amorphous boron :**

(i) Crystalline boron is steel grey or black coloured crystalline solid having a metallic lustre. Amorphous boron is brown powder.

(ii) Crystalline boron is inert in nature but amorphous boron is comparatively more active.

(iii) Crystalline boron is not attacked by air or oxygen even at high temperature. Amorphous boron is attacked by air or oxygen at 700°C.

(v) The specific gravity of crystalline form is 2·34 and that of amorphous form is 1·73.

(vi) Crystalline form is not attacked by oxidising acids (conc. H_2SO_4, HNO_3) but the amorphous form is attacked by these acids producing boric acid.

• Uses of boron :

(i) Boron carbide is used as abrasive and grinding materials. (ii) It is used in metallurgy for removing oxygen from molten metals. (iii) Ferro boron (20% B, 80% Fe) is used for making some special type of steel. (iv) It is used in medicine as boric acid and borax.

• Boron does not form B^{3+} ion—Explain why.

Boron forms only covalent compounds. The tendency of boron to form covalent compounds can be explained on the basis of polarisation power. According to Fajan's rule covalent bond is formed when the shape of the cation is very small and its charge is high. The tri-valent B^{3+} is very small and so it would exert large polarising effect on the neighbouring atoms. This would result in the transference of electrons from other atoms to boron ion which leads to the formation of covalent bonding by electron sharing. This explains why B^{3+} ion does not exist.

• The melting point of boron is very high—Explain why.

The structure of boron consists of a number of boron atoms. Each boron atom is strongly bonded with other boron atoms by strong covalent bond. Thus all the boron atoms are joined together by strong sigma bonds forming a giant molecule. Due to the extremely high strength of the covalent bonds holding numerous boron atoms together, boron is hard and a large amount of heat energy is needed to break so many covalent bonds of the giant molecule of boron. The explains the high melting point of boron.

• Boron nitride is called inorganic graphite—Explain why.

Like graphite, the structure of boron nitride consists of a number of two dimensional sheets like parallel layers of B and N atoms. These B and N atoms are arranged in a network of flat regular hexagons. Such layers of B and N-skeleton are arranged one above the other. The B and N atoms in the same layer are joined with each other by using sp^2 hybrid orbitals. The B—N bond distance is 1·45 Å. The C_6 hexagon in graphite and $(BN)_3$ hexagon in boron nitride are formed by same number of electrons. This is why boron nitride is called inorganic graphite.

3.4. Boric acid.

Orthoboric acid is commonly known as *boric acid* or *boracic acid*.

• Preparation of boric acid :

(1) **From mineral colemanite** ($Ca_2B_6O_{11}, 5H_2O$) **:**

Boric acid is prepared on a large scale from native *calcium borate* which is known as *colemanite*.

A stream of sulphur di-oxide is passed through a suspension of finely powdered colemanite in boiling water, when calcium sulphite and boric acid are produced.

On passing excess of sulphur di-oxide calcium sulphite is converted to soluble calcium bi-sulphite. The mixture is then cooled when boric acid crystallises out from the solution. It is separated by filtration. The boric acid thus obtained is washed with cold water and purified by recrystallisation from hot water.

$$Ca_2B_6O_{11} + 2SO_2 + 9H_2O = 2CaSO_3 + 6H_3BO_3$$
$$2CaSO_3 + 2SO_2 + 2H_2O = 2Ca(HSO_3)_2$$

(2) **Boric acid from borax :**

When a requisite quantity of concentrated hydrochloric acid or sulphuric acid is added to a hot and saturated solution of borax, boric acid is produced. After the completion of the reaction the product is cooled, when pearly white silky crystals of boric acid separate out. These are washed and purified by recrystallisation from hot water.

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3 \downarrow$$

● **Preparation of boron from (i) colemanite, (ii) borax and (iii) boric acid :**

Boric acid is first prepared from colemanite ore or from borax by the above mentioned process.

From colemanite—

$$Ca_2B_6O_{11} + 2SO_2 + 9H_2O = 2CaSO_3 + 6H_3BO_3$$
$$2CaSO_3 + 2SO_2 + 2H_2O = 2Ca(HSO_3)_2$$

From borax—

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$

In the next step, the boric acid thus produced is heated strongly when glass like transperant boron tri-oxide is obtained.

$$2H_3BO_3 = B_2O_3 + 3H_2O$$

The boron tri-oxide is then reduced by Mg at high temperature to produce Boron.

$$B_2O_3 + 3Mg = 3MgO + 2B$$

● **Properties of orthoboric acid :**

[A] Physical :

Orthoboric acid is soft silky and pearly white crystalline solid having a soft soapy touch. It is less soluble in cold water but its solubility increases with the rise of temperatures. Its specific gravity is 1·46. It is volatile in steam.

[B] Chemical :

(i) ***Acid property :*** Orthoboric acid is *very weak acid*—it is weaker than carbonic acid. Inspite of the presence of three hydrogen atoms in its molecule, it is monobasic acid i.e., only one hydrogen atom is replaceable. Its aqueous solution turns blue litmus wine red but it has no action on methyl orange. In its aqueous solution, it is ionised as H^+ and $H_2BO_3^-$ ions.

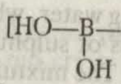
$$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$$

For this reason boric acid can not be titrated directly.

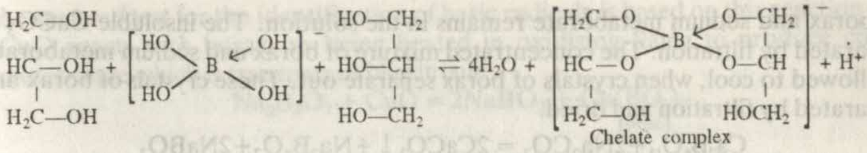
● **Boric acid can not be titrated against NaOH directly—Explain why.**

Orthoboric acid is very weak acid. Inspite of the presence of three hydrogen atoms in its molecule, only one hydrogen atom is replaceable and so it is monobasic. It can not change the colour of methyl orange. It is because of the fact that boric acid can not act as a proton doner like other acids, on the contrary, by accepting OH^- ion **it acts as a Lewis acid.**

$$H_3BO_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+ \qquad \text{........ (1)}$$
$$pK_a = 9{\cdot}0$$

The octet of boron in boric acid is not complete  $[HO{-}\underset{\underset{OH}{|}}{B}{-}OH]$, so in order to complete its octet, the B-atom of boric acid accepts electron pair from other atom or compound and thus acts as Lewis acid. For this reason boric acid can not be titrated against any alkali directly. It forms stable **chelate complex** with polyhydroxy organic compounds e.g., **glycerol, manitol** etc. Due to the formation of this stable complex, boric acid acts as a strong monobasic acid and hence can be titrated against NaOH.

With glycerol, $[B(OH)_4]$ produces the following stable chelate complex compound, equilibrium (1) shifts towards right, releasing one proton (H^+) and this proton neutralises NaOH.



(ii) ***Action on heat :*** On heating, orthoboric acid loses water in three successive steps.

(a) At 100°C it loses water forming *meta boric acid.*

$$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 + H_2O.$$

(b) At 140°C meta boric acid thus produced loses more water producing *pyro boric acid.*

$$4HBO_2 \xrightarrow{140^\circ C} H_2B_4O_7 + H_2O.$$

(c) At red hot condition it loses all water producing a glassy mass of *boron tri-oxide.*

$$H_2B_4O_7 \xrightarrow{\text{red hot}} 2B_2O_3 + H_2O$$

(iii) Boric acid when treated with *methyl* or *ethyl alcohol* methyl or ethyl borate (ester) is produced. This ester is volatile and so on heating, the produced vapour of this ester burns with green edged flames on ignition.

$$\underset{\text{Ethyl borate}}{H_3BO_3 + 3C_2H_5OH = B(OC_2H_5)_3 + 3H_2O} \qquad \underset{\text{Methyl borate}}{H_3BO_3 + 3CH_3OH \rightarrow B(OCH_3)_3 + 3H_2O}$$

(iv) *Action on Ammonium bifluoride :*

Finely powdered boric acid when fused with colourless crystalline *ammonium bifluoride*, solid ***ammonium tetra fluoro borate (III)*** is formed.

$$H_3BO_3 + 2NH_4HF_2 = NH_4BF_4 + NH_3 + 3H_2O$$

When the mixture is heated beyond the fusion temperature a mixture of gases are formed. No solid is left as residue.

$$2H_3BO_3 + 3NH_4HF_2 = 3NH_3 + 6H_2O + 2BF_3$$

Strong alkali KOH is produced by the reaction of 2 acidic compounds H_3BO_3 and KHF_2.

$$H_3BO_3 + 2KHF_2 = KOH + KBF_4 + 2H_2O$$

● **Uses of boric acid :** (i) Boric acid is used in medicine as an antiseptic. It is also used for preparing borated cotton, boric ointment etc. (ii) Very dilute solution of boric acid is used as eye lotion. (iii) It is used in the manufacture of borax, glass and glazes in enamel industries. (iv) It is used for the preservation of food.

● **Tests for boric acid and borate**—To identify the presence of boric acid in a sample of borate.

(i) The sample is mixed with methyl alcohol in a test tube. The test tube is then heated gently and the vapour coming out of it is ignited. The issuing vapours burn with a green edged flame.

Boric acid reacts with methyl alcohol to produce methyl borate—a volatile ester, which on ignition burns with a green edged flame.

$$H_3BO_3 + 3CH_3OH = B(OCH_3)_3 + 3H_2O$$

(ii) In case of borate, only addition of CH_3OH would not produced green edged flame like boric acid. In this case, a paste of borate and **conc. H_2SO_4** is taken in a test tube and a little methyl alcohol is added to it. The mixture is then gently heated and the vapour coming out of it is ignited. The issuing vapours burn with green edged flame.

$$Ca(BO_2)_2 + H_2SO_4 + 2H_2O = CaSO_4 + 2H_3BO_3$$

$$H_3BO_3 + 3CH_3OH = B(OCH_3)_3 + 3H_2O$$

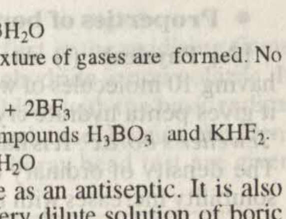


Fig 3.1

3.5 Borax or Sodium Pyroborate or Sodium tetra borate.

In Bengal borax is known as '***Sohaga***'. Crude borax occurs in nature as ***tincol*** which is found in Tibet and Cylone.

● **Preparation of borax :**

(i) ***From colemanite*** : Finely powdered *colemanite* is treated with *boiling sodium carbonate* solution when insoluble *calcium carbonate* is precipitated and a mixture of borax and sodium metaborate remains in the solution. The insoluble $CaCO_3$ is separated by filtration. The concentrated mixture of borax and sodium metaborate is allowed to cool, when crystals of borax separate out. These crystals of borax are separated by filtration and dried.

$$Ca_2B_6O_{11}+2Na_2CO_3 = 2CaCO_3\downarrow + Na_2B_4O_7+2NaBO_2$$

To have further yield, carbon di-oxide is passed through the mother liquor containing sodium metaborate, when sodium metaborate is converted to borax.

$$4NaBO_2+CO_2 = Na_2B_4O_7+Na_2CO_3$$

(ii) ***From boric acid*** : When a solution of *boric acid is boiled with sodium carbonate*, borax is produced. The solution containing borax is made concentrated by evaporation and then cooled, when crystals of borax separate out from the solution which are separated by filtration.

$$4H_3BO_3+Na_2CO_3 = Na_2B_4O_7+CO_2+6H_2O$$

(iii) ***From tincal*** : The mineral tincal ($Na_2B_4O_7$) contains about 55% borax. Finely powdered tincal is treated with boiling water and filtered. The filtrate is made concentrated. The concentrated solution is then cooled when almost pure borax separates out as crystals.

- **Properties of borax :**

[A] **Physical :** (i) At ordinary temperature borax forms transparent crystals having 10 molecules of water of crystallisation (ii) When crystallised at above 65°C it gives penta hydrate crystals ($Na_2B_4O_7, 5H_2O$). This variety of borax is known as *'Jeweller's borax'*. It is harder than ordinary borax and does not effloresce in air (iii) The density of ordinary borax is 1·72. (iv) Borax is fairly soluble in water and the solubility increases with the rise of temperatures.

[B] **Chemical :**

(i) ***Aqueous solution of borax is alkaline*** : The aqueous solution of borax is alkaline in reaction because borax undergoes hydrolysis yielding a mixture of sodium hydroxide and boric acid. As sodium hydroxide is a strong alkali and H_3BO_3 a weak acid, the final solution exhibits alkaline properties.

$$\begin{array}{lcl} Na_2B_4O_7 + 3H_2O & \rightleftharpoons & 2NaBO_2 + 2H_3BO_3 \\ 2Na_2BO_2 + 4H_2O & \rightleftharpoons & 2NaOH + 2H_3BO_3 \\ \hline Na_2B_4O_7 + 7H_2O & \rightleftharpoons & 4H_3BO_3 + 2NaOH \end{array}$$

The aqueous solution of borax gives a violet red colour with phenolpthalein due to the hydrolysis of borax. The hydrolysis of borax can he prevented if glycerol is added to the solution. Thus when phenolpthalein is added to an aqueous solution of borax, a pink colour develops but when glycerol is added to it, the pink colour is discharged. This is due to the fact that glycerol with boric acid produces a complex compound releasing one proton (H^+) and this proton neutralises NaOH. Thus the solution becomes neutral again and as a result the solution becomes colourless again.

(iii) ***Action of heat*** : Borax swells up on heating due to the evaporation of water of crystallisation from its molecule. On stronger heating the mass melts and ultimately forms a transparent glass like mass which is composed of *sodium metaborate* and *boron tri-oxide*.

$$Na_2B_4O_7 = 2NaBO_2 + B_2O_3$$

These two compounds on being heated with some metallic salts, form coloured metallic metaborates, the colour of which varies with the nature of metals. The *borax bead* test for the identification of basic radicals is based on this reaction e.g., CuO reacts with borax on being heated in oxidising flame to produce copper metaborate which is transparent blue in cold.

$$Na_2B_4O_7 + CuO = 2NaBO_2 + \underset{\text{(blue)}}{Cu(BO_2)_2}$$

• **Borax bead test :** This test is applied for the identification of basic radicals. A small circular loop is made at the free end of a clean platinum wire which is attached to a glass rod. The loop is at first heated in a bunsen flame (non luminous) and is dipped in powdered borax. At this small quantity of borax adheres to the loop of the platinum wire.

The loop with the borax is heated again, when borax swells up, loses water and then fuses to give a colourless glassy bead on the loop. This colourless transparent bead is made of sodium metaborate and boric anhydride B_2O_3.

$Na_2B_4O_7, 10H_2O \rightarrow Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3$

The hot bead is then touched with a little of the coloured metallic salt whose metallic radical is to be identified. A minute quantity of the salt adheres to the bead. Now the bead along with the salt is heated first in the oxidising flame and then in the reducing flame of the burner. As boric anhydride is non volatile. It displaces the more volatile acidic part of the salt and combines with the basic radical to form metaborate. The colour of the bead is noted in each case. During the identification of some basic radicals the observations of the borax bead test are given below :

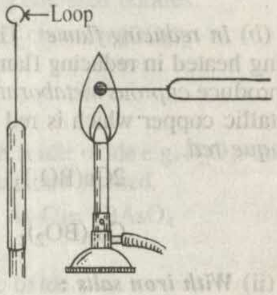


Fig 3.2

Metallic radicals	The colour of the bead	
	In oxidising flame	In reducing flame
(1) Copper	Transparent green when hot Transparent blue when cold	Opaque red
(2) Iron	Reddish yellow when hot Yellow when cold	Bottle the green when cold or hot
(3) Cobalt	Deep blue	Deep blue
(4) Manganese	Ame thyst	Colourless
(5) Chromium	Green	Green

• **Chemical reactions involved in borax bead test :**

Being heated in the loop borax melts to form a glass like transparent bead which is composed of *sodium metaborate* and *boron tri-oxide.*

$$Na_2B_4O_7, 10H_2O = Na_2B_4O_7 + 10H_2O \uparrow$$
$$Na_2B_4O_7 = 2NaBO_2 + B_2O_3 \uparrow$$

When Cu, Fe, Co, Cr salts are heated with the bead the salts are decomposed at first to give their respective oxides. These oxides react with B_2O_3 of the bead to form the respective metaborate compounds having different colours.

Examples :

(i) ***With copper salts :***

(a) *In oxidising flame :* Copper salts on being heated in oxidising flame, are converted to cupric oxide.

$$CuSO_4.\,5H_2O = CuSO_4 + 5H_2O$$
$$2CuSO_4 = 2CuO + 2SO_2 + O_2$$

The CuO thus produced combines with B_2O_3 of the bead to produce a *copper metaborate,* the colour of which is *transparent green when hot* and *transparent blue when cold.* By observing the colour of the bead the metallic radical is identified.

$$CuO + B_2O_3 = \underset{\text{Copper meta borate}}{Cu(BO_2)_2}$$

Some orthoborate is also produced.

$$CuO + NaBO_2 = \underset{\text{Sodium copper orthoborate}}{NaCuBO_3}$$

(*b*) *In reducing flame :* The blue transparent bead containing cupric metaborate on being heated in reducing flame, is reduced by the fine particles of carbon of the flame to produce *cuprous metaborate*. The colourless cuprous metaborate is further reduced to metallic copper which is red in colour. Thus in the *reducing flame the bead becomes opaque red.*

$$2Cu(BO_2)_2 \;+\; C \;=\; \underset{\text{Cuprous metaborate}}{Cu_2(BO_2)_2} \;+\; B_2O_3 + CO$$
$$Cu_2(BO_2)_2 \;+\; C \;=\; \underset{\text{red}}{2Cu} + B_2O_3 \;+\; CO$$

(ii) ***With iron salts :***

(*a*) *In oxidising flame :*

Iron salts on being heated strongly in the oxidising flame are converted to ferric oxide. The ferric oxide thus produced combines with B_2O_3 to produce *ferric metaborate* the colour of which is *reddish yellow when hot* and *yellow when cold.*

$$Fe_2O_3 + 3B_2O_3 = \underset{\text{Ferric metaborate (yellow)}}{2Fe(BO_2)_3}$$

(*b*) *In reducing flame :* The yellow bead of ferric metaborate on being heated in a reducing flame, is reduced to *ferrous metaborate* the colour of which is *bottle green.*

$$2Fe(BO_2)_3 + C = \underset{\substack{\text{Ferrous meta borate}\\\text{(bottle green)}}}{2Fe(BO_2)_2} + B_2O_3 + CO$$

- **Uses of borax :**

(i) Borax is used in the preparation of glazes for the earthenware, porcelain, enamels.
(ii) It is used as flux in welding and soldering of metals.
(iii) It is used in the laboratory for the identification of the metallic radicals.
(iv) It is used in the preparation of pyrex glass, antiseptic soap and in stiffing the candle wicks.

3.6. Boron Sesquioxide (B_2O_3).

The term sesqui means one and a half. Hence Boron sesquioxide should have a formula $BO_{1\frac{1}{2}}$ or B_2O_3. Al, Ga, In and Tl also form sesquioxides of the formula M_2O_3.

Preparation :

B_2O_3 exists in two forms (i) Crystalline form and (ii) Glassy form. The glassy form of B_2O_3 is obtained either by dehydrating Boric acid. (or by burning Boron in oxygen gas.)

$$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{\text{Red heat}} B_2O_3$$
$$4B + 3O_2 = 2B_2O_3$$

When meteboric acid is dehydrated under reduced pressure and the temperature is slowly raised to 400°C for a prolonged period, crystalline B_2O_3 is formed.

Properties :—(1) It is a white solid oxide. Glassy B_2O_3 does not have sharp melting point while cystalline variety melts at 450°C.

(2) It is hygroscopic and slowly absorbs water to form boric acid. Hence B_2O_3 is called boric anhydride.

$$B_2O_3 \xrightarrow{+H_2O} \underset{\text{Meta boric acid}}{2HBO_2} \xrightarrow{+H_2O} \underset{\text{Ortho boric acid}}{H_3BO_3}$$

Hence Boric oxide is an acidic oxide.

When fused with alkalis it forms salt and water. $2NaOH + B_2O_3 = 2NaBO_2 + H_2O$

With transitional metal oxides it forms corresponding coloured borates.

$$Cr_2O_3 + 3B_2O_3 = \underset{\text{(green)}}{2Cr(BO_2)_3} \qquad CoO + B_2O_3 = \underset{\text{(blue)}}{Co(BO_2)_2}$$

$$Fe_2O_3 + 3B_2O_3 = \underset{\text{(yellow)}}{2Fe(BO_2)_3}$$

(3) Boric oxide has mild basic property also. Thus with acidic oxide e.g. P_2O_5, As_2O_5 and SO_3 corresponding phosphate, arsenate and bisulphate are formed.

$$B_2O_3 + P_2O_5 = 2BPO_4 \qquad B_2O_3 + As_2O_5 = 2BAsO_4$$

$$B_2O_3 + 3H_2O + 6SO_3 = 2B(HSO_4)_3$$

These reactions show the amphoteric nature of boric oxide.

(4) When a mixture of B_2O_3, CaF_2 and conc H_2SO_4 is strongly heated, colourless vapours of BF_3 are liberated.

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O$$

(5) When dry Cl_2 gas is passed over a mixture of red hot finely divided B_2O_3 and coke, gaseous BCl_3 is escaped which may be condensed to a liquid in a freezing mixture.

$$B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO$$

With Br_2— $$B_2O_3 + 3C + 3Br_2 = \underset{\text{(vapour)}}{2BBr_3} + 3CO$$

(6) When B_2O_3 is heated with KCN or $Hg(CN)_2$ the product is boron nitride.

$$B_2O_3 + 2KCN = 2BN + 2CO + K_2O$$

$$B_2O_3 + Hg(CN)_2 = 2BN + CO + CO_2 + Hg$$

(7) Other important reaction of B_2O_3 are—

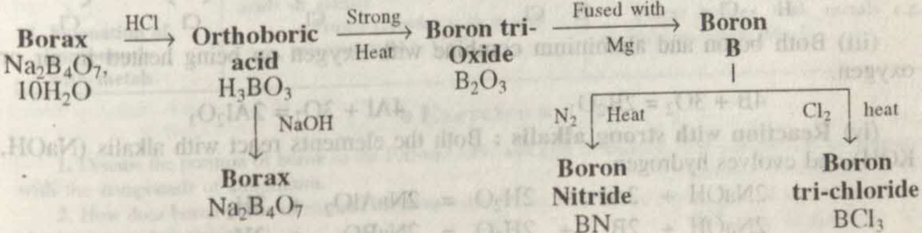
$$B_2O_3 + 6KBF_4 + 3H_2SO_4 = 3K_2SO_4 + 8BF_3 + 3H_2O$$

$$B_2O_3 + 3PCl_5 = 2BCl_3 + 3POCl_3$$

$$B_2O_3 + 2NH_3 = 2BN + 3H_2O$$

Uses : It is mainly used in the manufacture of glass, ceramics and pottery.

• Chart showing the preparation of different compounds of boron starting from borax :



• Tests for the identification of borax, boric acid and borates :

Boron is generally tested as borax, boric acid or borates.

Experiments	Observations
(i) Flame test.	
(a) A platinum wire after moistioning in conc. H_2SO_4. is made to touch with a little borate, or boric acid and CaF_2 and then heated in the non luminous flame.	A green flame is produced. $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$ $Na_2B_4O_7 + H_2SO_4 = 2B_2O_3 + Na_2SO_4 + H_2O$ $B_2O_3 + 6HF = 2BF_3 \uparrow + 3H_2O$
(b) In a porcelain basin a mixture of ethyl alcohol, borax or borate salt or H_3BO_3 and conc. H_2SO_4 is taken and ignited.	The mixture is found to burn with green edged flame. $Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4$ $H_3BO_3 + 3C_2H_5OH = B(OC_2H_5)_3 + 3H_2O$
(ii) Cobalt nitrate test. A small amount of borate or boric acid or borax is taken in the cavity of a charcoal block and heated in the oxidising flame and then 2 drops of cobalt nitrate solution is added to the residue and heated again in the oxidising flame.	The colour of the residue in the cavity of the charcoal block turns blue.
(iii) Wet test. To a neutral solution of a borate salt, $AgNO_3$ solution is added.	A white precipitate of silver metaborate is obtained. $Na_2B_4O_7 + 2AgNO_3 + 3H_2O = 2AgBO_2 + 2NaNO_3 + 2H_3BO_3$
The precipitate is boiled with water.	The white precipitate turns black due to formation of Ag_2O. $2AgBO_2 + 3H_2O = Ag_2O + 2H_3BO_3$

• Comparison of the properties of boron and aluminium :

Boron and aluminium occupy Group III B in the periodic table. Inspite of being the members of the same group, they have very slight resemblance with each other. Boron, however, shows much resemblance with silicon, an element of Group IV to which it is diagonally related.

$$\begin{tikzcd}
\text{II} \arrow[r, dash] & \text{III} \arrow[r, dash] & \text{IV} \\
{}_4\mathbf{Be} & {}_5\mathbf{B} \arrow[dr] & {}_6\mathbf{C} \\
{}_{12}\mathbf{Mg} & {}_{13}\mathbf{Al} & {}_{14}\mathbf{Si}
\end{tikzcd}$$

Points of similarity :

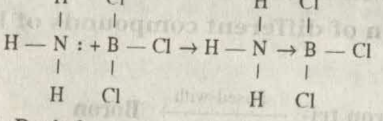
(i) Electronic configuration. Both have three electrons in the valency shell and the penultimate orbit is complete with 2 electrons in boron and 8 in the case of aluminium.

Boron (5) $1s^2 \quad 2s^2 \quad 2p^1$

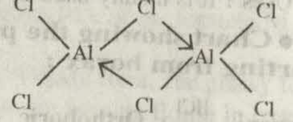
Aluminium (13) $1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^1$

Both are trivalent.

(ii) Both the elements exhibit a covalency of 3 in their halides. These halides act as acceptors when ever donor molecules are available.



$H_3N: + BCl_3 \rightarrow H_3N \rightarrow BCl_3$



(iii) Both boron and aluminium combine with oxygen on being heated in air or oxygen.

$$4B + 3O_2 = 2B_2O_3 \qquad 4Al + 3O_2 = 2Al_2O_3$$

(iv) **Reaction with strong alkalis :** Both the elements react with alkalis (NaOH, KOH) and evolves hydrogen.

$$2NaOH + 2Al + 2H_2O = 2NaAlO_2 + 3H_2$$
$$2NaOH + 2B + 2H_2O = 2NaBO_2 + 3H_2$$

(v) Boron and aluminium react with chlorine producing their respective chlorides. Both the chlorides are covalent and are easily hydrolysed by water.

(vi) Both of these elements combine with nitrogen producing nitrides which undergo hydrolysis liberating ammonia.

$$2B + N_2 = 2BN \qquad BN + 3H_2O = NH_3 + H_3BO_3$$
$$2Al + N_2 = 2AlN \qquad AlN + 3H_2O = NH_3 + Al(OH)_3$$

Points of difference :

(i) Boron is a typical non metal whereas aluminium is a metal.

(ii) Boron is a bad conductor of electricity whereas aluminium is a good conductor.

(iii) Boron exhibits allotropy but aluminium does not.

(iv) Boron forms compounds by covalency. In gaseous state, though aluminium compounds are covalent but ionises in aqueous solution.

(v) Boron forms a number of stable hydrides. Aluminium does not form any stable hydride.

(vi) B_2O_3 is an acidic oxide but Al_2O_3 is an amphoteric oxide.

$$B_2O_3 + 3H_2O = 2H_3BO_3$$

(vii) Dilute hydrochloric acid liberates hydrogen with aluminium but boron has no action on this acid.

(viii) BCl_3 is a gas at ordinary temperature. It is converted to a colourless liquid when cooled. $AlCl_3$ is solid and sublimes on heating.

• Comparison of carbon and boron •

Properties	Carbon	Boron
1. Allotropy	A non-metal-exhibits allotropy. It has two types of allotropes— crystalline and amorphous.	A non-metal-exhibits allotropy. It has two types of allotropes—crystalline and amorphous.
2. Melting Point	Very High = 3600°C	High = 2300°C.
3. Action on air	On combustion in air CO_2 is produced.	On combustion in air B_2O_3 and BN are produced.
4. Action on acids	Graphite is oxidised by nitric acid to form graphitic acid.	HNO_3 or conc. H_2SO_4 oxidises boron to form boric acid.
5. Nature of oxides	CO_2 is a gas and an acidic oxide. CO is a gas and neutral oxide.	B_2O_3 is glass like solid. It slowly dissolves in water forming boric acid.
6. Nature of halides	CF_4 is an inert gas, CCl_4 is almost a liquid, both are stable in water.	BF_3 is a gas and BCl_3 is a liquid, both are hydrolysed in aqueous solution.
7. Nature of hydrides	CH_4, C_2H_6 etc., hydro-carbons are not active. These are not attacked by acids or alkalis.	B_2H_6. B_3H_7 etc., are decomposed by water.
8. Formation of compounds with metals	Forms carbides with metals e.g., calcium carbide CaC_2.	Forms borides with metals e.g., magnesium boride Mg_3B_2.

• Exercise •

1. Discuss the position of boron in the Periodic table and give an account of its compounds as compared with the compounds of aluminium. [*Delhi*—'75. *Cal. B.Sc.* '72]

2. How does boron occur in nature? Mention some of the minerals of boron. How is amorphous boron obtained from born trioxide? [*H.S.* '96] [*Agra B.Sc.* '65]

3. How is crystalline boron prepared? Mention the important properties and uses of boron.

4. How is borate radical detected in presence of copper? Illustrate the reducing property of boron.

5. Excepting diamond name the hardest substance and describe how is this prepared. What happens when a copper salt is heated with borax bead in a platinum wire? Give the equations of the chemical reactions involved in the process.

6. How is boric acid prepared from—(a) borax [*H.S. '97*] (b) from colemanite? [*H.S. 97*][*I.A.S. '89*]

7. Starting from boric acid how will you get (i) boron anhydride, (ii) boron tri-choloride, (iii) boron. [*Punjab B.Sc. '69*]

8. Write down the formula and chemical name of borax. How does borax occur in nature? How is borax prepared? Mention its properties and uses. [*Jt. Ent. '90*]

9. Starting from borax how would you obtain (i) boron nitride, (ii) boron trioxide, (iii) boron trichloride. Discuss the chemistry of borax bead test. [*Madras B.Sc. '76, Kanpur '78*]

10. How borax is converted to boric acid and vice versa? Starting from borax how would you prepare (i) boron hydride, (ii) boron?

11. What is borax bead test? Discuss the chemistry involved in the borax bead test with suitable examples. Compare the properties of boron with those of carbon. [*Gauhati B.Sc. '70*]

12. (a) Compare the properties of boron with those of aluminium.

(b) How will you distinguish between borax and boric acid by a single chemical test? [*Jt Ent. '96*]

(c) How is orthoboric acid detected? [*H.S. '91*]

13. Explain why—

(i) Boric acid can not be directly titrated against sodium hydroxide.

(ii) Aqueous solution of borax is alkaline. [*H.S. '91*]

(iii) Boric acid is very weak acid, but it acts as a strong acid in presence of glycerol.

(iv) Boron can not be obtained by reducing B_2O_3 by carbon.

(v) Borax when heated swells up at first and then melts to a glassy mass. [*H.S. '92*]

(vi) Boron nitrate can not be prepared by the actions of nitric acid on boron.

(vii) Boron like N_2 combines with metals to form borides.

(viii) Boric acid is not titrated against NaOH directly. [*Jt. Ent. '91*]

(ix) Inspite of the presence of 3 hydrogen atoms, boric acid is a monobasic acid.

(x) A mixture of methyl alcohol and boric acid on ignition produces green edged flame.

(xi) To an aqueous solution of borax when phenolpthelein is added, the solution turns pink, but on addition of glycerol the solution decolourises.

(xii) Boron halides are typical Lewis acids.

(xiii) The B—F bond distance in BF_3 is less than in $NaBF_4$.

(xiv) BF_3 is less acidic then BCl_3.

(xv) Boron can not produce B^{3+} ion.

(xvi) The melting point of boron is very high.

(xvii) The aqueous solution of boron halide is acidic.

(xviii) Boron forms covalent compound.

(xix) Although the I.P. of Boron is less than gold, yet former is a non metal while latter is a metal.

(xx) While Al can forms $[AlF_6]^{3-}$ but boron can not form $[BF_6]^{3-}$.

14. What happens when—

(i) Orthoboric acid is gradually heated.

(ii) B_2O_3 and ferric oxide are heated in oxidising flame. [*H.S. '91*]

(iii) A mixture of boron and sodium hydroxide is fused at high temperature. [*H.S. '89*]

(iv) A mixture of boric acid and methyl alcohol is distilled and the product obtained is reacted with caustic soda solution. [*Jt Ent. '87*]

(v) Boron is reacted with conc. nitric acid and conc. H_2SO_4 separately.

(vi) Colemanite is boiled with Na_2CO_3 solution. [*H.S. '98*]

(vii) Borax is gradually heated to high temperature.

(viii) Copper is heated with borax in oxidising flame.

(ix) Boric acid is boiled with methanol. [*H.S. '99*]

(x) A mixture of boron tri-oxide and Mg powder is fused by heating and the product obtained is boiled with dil. HCl. The residue thus obtained is reacted with super-heated steam. [*H.S. '92*]

15. (a) Name a compound in which one atom has electron less than 8. [*Jt. Ent., '92*]

(b) Write down the chemical principle of borax bead test. [*H.S. 2000*]

(c) Name a compound which is as hard as diamond.

(d) Name a nitride whose electrical conductivity is 10 times than the metal it contains.

(e) How do you prepare borax from colemanite. [H.S. 2000]

(f) What is inorganic benzene? Write its structure. [Jt Ent. 2000]

16. Cite a reaction where an alkali is formed from two acidic substances. [Jt Ent. '99]

17. How would you prepare boron from boric acid? [H.S. '94]

18. What happens when

(i) Boric acid is heated upto 140°C. [H.S. '98]

(ii) A small amount of borate or borax is taken in the cavity of a charcoal block and heated in an oxidising flame and then 2 drops of cobalt nitrate solution is added to the residue and heated again in oxidising flame.

(iii) Conc. H_2SO_4 is added to a mixture of boric acid and calcium fluoride and the mixture is heated.

19. (i) How is boric acid distinguished from borate salt? [H.S. '98]

(ii) Boron nitride is called inorganic graphite—explain why.

(iii) Identify *A, B, C* and *D*—

$$\text{Colemanite} \xrightarrow[\text{excess}]{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[1200°C]{NH_4Cl} C \xrightarrow{HF} D$$

Ans. (A) = Boric acid (H_3BO_3), *(B)* = borax ($Na_2B_4O_7$), *(C)* = Boron nitride (BN), *(D)* = Ammonium tetra fluoroborate (III) (NH_4BF_4)

20. Give the correct answer :—

(i) The colour of the borax bead produced by iron salts is—(a) blue (b) opaque red (c) bottle green (d) yellow. [*Ans.*: c, d]

(ii) Borax when heated swells up because—(a) it loses water of crystallisation (b) CO_2 is given off (c) due to heat. [*Ans.*: a]

(iii) $Na_2B_4O_7$, $10H_2O$ is the formula of—(a) ulexite (b) colemanite (c) borax. [*Ans.*: c]

(iv) The name inorganic graphite is given to—(a) Boron nitride (b) Boron tri-fluoride (c) boron tri-oxide (d) borax. [*Ans.*: a]

(v) Borax is a—(a) metal (b) non metal (c) metalloid (d) compound. [*Ans.*: b]

(vi) On the addition of mineral acid to an aqueous solution of borax, the compound formed is (a) Boron hydride (b) Orthoboric acid (c) Metaboric acid (d) Pyroboric acid. [*Ans.*: b, *Roorkee '92*]

(vii) Which one is metaboric acid?

(a) HBO_2 (b) $H_2B_4O_7$ (c) H_3BO_3 (d) $B(OH)_3$ [*Ans.*: a]

(viii) Which of the following compounds are formed when BCl_3 is treated with water?

(a) H_3BO_3 + HCl (b) B_2H_6 + HCl (c) B_2O_3 + HCl (d) None of the above. [*Ans.*: a]

(ix) Which one of the following is most abundant in the earth's crust?

(a) B (b) Al (c) In (d) Tl [*Ans.*: b; *BHU. '79, '81*]

(x) Which one of the following exhibits Inert Pair effect?

(a) Al (b) Tl (c) B (d) S [*Ans.*: b; *AIIMS '82*]

21. A certain salt (X) gives the following tests—

(i) Its aqueous solution is alkaline to litmus.

(ii) On strongly heating it swells to give a glassy material.

(iii) When concentrated H_2SO_4 is added to a hot concentrated solution of *(X)*, white crystals of a weak acid separates out.

Identify *(X)* and write down the chemical equations for steps (i), (ii) and (iii). [*Roorkee '92*]

Ans. $X = Na_2B_4O_7 . 10H_2O$ (Borax)

(i) $Na_2B_4O_7 + 7H_2O \longrightarrow H_3BO_3 + 2NaOH$

(ii) $Na_2B_4O_7 . 10H_2O \longrightarrow Na_2B_4O_7 + 10H_2O$

$Na_2B_4O_7 \longrightarrow 2Na_2BO_2 + B_2O_3$

(glassy bead)

(iii) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$

(weak boric acid)

22. (i) A white precipitate *(B)* is formed when a mineral *(A)* is boiled with Na_2CO_3 solution.

(ii) The precipitate is filtered and the filtrate contains two compounds *(C)* and *(B)*. The compound *(C)* is removed by crystallisation and when CO_2 gas is passed through the mother liquor left *(D)* changes to *(C)*.

(iii) The compound *(C)* on strong heating gives two compounds *(D)* and *(E)*.

(iv) *(E)* on heating with Cobalt oxide produces blue coloured substance *(F)*.

Identify *A* to *F* and give chemical equations for the reaction at steps (i) to (iv). [*Roorkee, '95*]

Ans. *A* is the mineral colemanite $Ca_2B_6O_{11}$

$B = CaCO_3$, $C = Na_2B_4O_7$, $D = NaBO_2$ $E = B_2O_3$ $F = Co\,(BO_2)_2$

Reactions :—

$$\underset{(A)}{Ca_2B_6O_{11}} + 2Na_2CO_3 = \downarrow \underset{(B)}{CaCO_3} + \underbrace{Na_2B_4O_7 + 2NaBO_2}_{\text{soluble}}$$

$$4NaBO_2 + CO_2 = \underset{(C)}{Na_2B_4O_7} + Na_2CO_3$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underset{(D)}{2NaBO_2} + \underset{(E)}{B_2O_3}$$

$$CoO + B_2O_3 \xrightarrow{\Delta} \underset{\text{Cobalt metaborate—deep blue bead } (F)}{Co\,(BO_2)_2}$$

Carbon and its compounds 4

Symbol—C **Atomic weight—12** **At. number—6** **Oxidation numbers—+2, +4**
Electronic configuration—$1s^2 . 2s^2 . 2p^2$. **Position in the periodic table—IVB.**

4.1. Occurrence.

Carbon is found in nature in free state as well as in the form of compounds.

(i) *In free state,* it occurs in nature in crystalline form as *diamond* and *graphite.*

(ii) *Coal* contains some elements like As, S, P, etc., along with some complex compounds of carbon.

(iii) *As carbonates,* carbon occurs in sedementary rocks as *lime stone* ($CaCO_3$), *dolomite,* ($CaCO_3$, $MgCO_3$), *calamine* ($ZnCO_3$), *spathic iron ore* ($FeCO_3$) etc.

(vi) In combination with other elements it is found in *mineral oils, marsh gas* and *natural gas* as hydrocarbons. It is an essential constituent of animal and plant *tissues.* It is found as *carbohydrates* e.g, *starch, sugar, cellulose* and as *proteins* which occurs in plants and animals.

(v) It also occurs in air as *carbon di-oxide.*

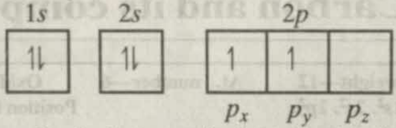
• Coal and Carbon :

Coal is a complex carbonacious mineral which is dark brown or black colour. It is of vegetable origin. The vast dense forests on earth in the remote past were submerged under ground due to earthquake and other natural phenomenon. In course of time these vegetable matters under the influence of high pressure and temperature along with the action of some bacteria present there, passed through a series of chemical changes and finally converted into coal. During these series of decomposition some portions of carbon, hydrogen and oxygen were eliminated as CO_2, H_2O and CH_4 and thus the residue became increasingly rich in carbon. The different types of coal with their names and carbon contents are given below :—

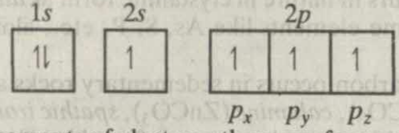
Name	Ratio of C, H and O by wt.	Calorific value	Uses
1. Peat	C = 60% H = 5·9% O = 34·1%	9900 B. Th. U/c.ft	Low grade coal produces much soot on combustion. It is less used as fuel.
2. Lignite	C = 67% H= 5·2% O = 27·8%	11700 B. Th. U/c. ft	Low grade coal produces much soot when when ignited. It is less used as fuel.
3. Bituminous coal	C = 88.4% H = 5·6% O = 6%	14950 B. Th. U/c. ft	High grade soft coal—produces less smoke on combustion. As its calorific value is high, it is used as fuel and in producing coal gas.
4. Anthracite	C = 94·1% H = 3·4% O = 2·5%	15720 B. Th. U/c. ft	Very high grade coal—produces less smoke when ignited. It is used as reducing agent in the extraction of metals.

4.2. Characteristics of Carbon atom.

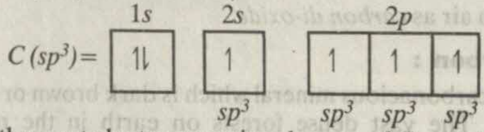
(i) Carbon is the first member of Group IV B in the periodic table. The electronic arrangements of carbon atom is $1s^2, 2s^2, 2p^2$. The distribution of electrons in the orbital is represented by—



As there are two unpaired electrons in its '*p*' orbital, carbon should exhibit valency of two. But in excited state one of the electrons of '2*s*' orbital jumps from '2*s*' to vacant $2p_z$ orbital and thus the electronic arrangement in carbon atom becomes



With this new arrangements of electrons there are four unpaired electrons and so carbon atom can form 4 covalent bonds. Though one of the bonds involves one '*s*' orbital, and 3 others of the '*p*' orbital, the 4 bonds are all equivalent (*sp^3 hybridisation—four sp^3 hybrid orbitals.*)



(ii) Carbon is the most electro-negative element of Group IV B. Its electronegativity is 2·5. As it occupies the mid-position in the periodic table, carbon is able to combine with the electropositive as well as with the electronegative elements. It combines with electro-positive elements like hydrogen to form methane and electronegative elements like chlorine to form carbon tetrachloride (CCl_4).

(iii) Carbon atom has the unique capacity of combining with a large number of other carbon atoms to form chains or rings of carbon atoms. This property of carbon atom is known as *Catenation*. Due to this property of carbon atom, there exists a huge number of carbon compounds of different types.

(iv) The high melting point of carbon (3930°C) results from the very stable arrangement of diamond type of lattice,—high heat energy is required to break the numerous covalent bonds in it during its melting.

4.3. Allotropy and allotropic modifications of elements.

• Allotropy :

There are some elements which can exist in two or more different forms having different physical properties but same chemical properties.

The property of an element to exist in two or more different forms which have different physical properties but the same chemical properties, is known as allotropy.

The different forms of such elements are called allotropic forms or allotropic modifications of the element.

The allotropy results from—(i) a difference in the arrangement of the atoms in the crystalline structure, (ii) a difference in the number of atoms in the molecules as in the case of oxygen (O_2) and ozone (O_3), (iii) a difference in the available energy as in the case of rhombic sulphur and monoclinic sulphur. Rhombic sulphur is converted to monoclinic sulphur only by the application of heat. Consequently monoclinic sulphur contains more available energy than that of rhomic sulphur.

4.4. Allotropy of Carbon.

Carbon exists in two allotropic forms—(i) *Crystalline form,* (ii) *Amorphous form.*

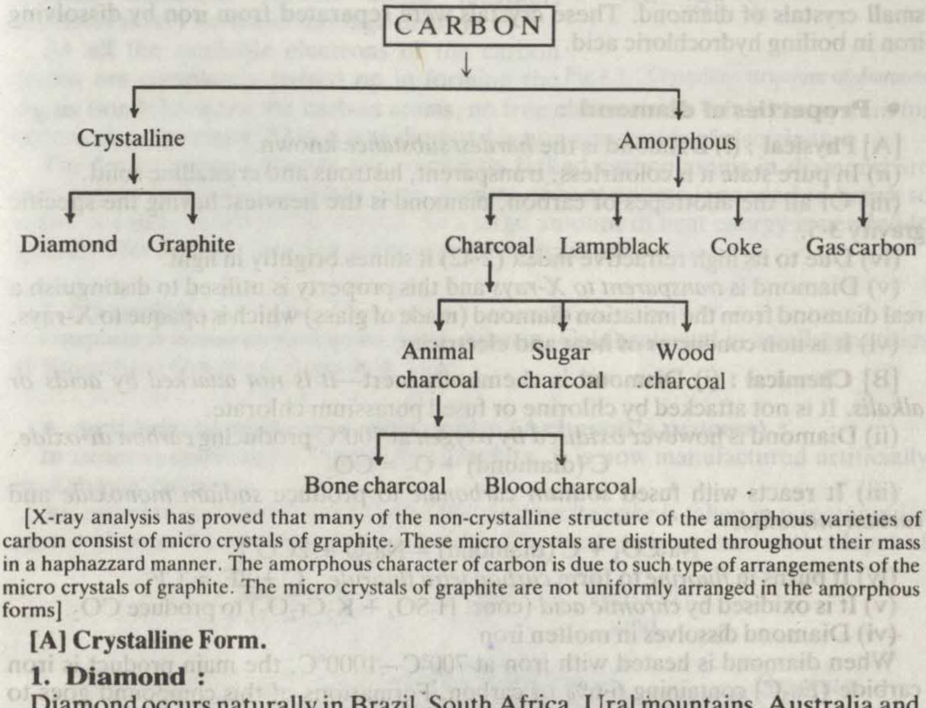
[A] The crystalline form of the allotropes of carbon includes —(a) **Diamond,** (b) **Graphite.**

[B] The amorphous form of allotropes of carbon includes—(a) **Charcoal,** (b) **Lampblack,** (c) **Coke,** (d) **Gas carbon.**

There are three varieties of charcoal depending upon the source, such as—(i) **Wood charcoal,** (ii) **Sugar charcoal** and (iii) **Animal charcoal.**

Two varieties of animal charcoal are there : (i) **Bone charcoal,** (ii) **Blood charcoal.**

The different allotropes of carbon are shown in the following chart.



[X-ray analysis has proved that many of the non-crystalline structure of the amorphous varieties of carbon consist of micro crystals of graphite. These micro crystals are distributed throughout their mass in a haphazzard manner. The amorphous character of carbon is due to such type of arrangements of the micro crystals of graphite. The micro crystals of graphite are not uniformly arranged in the amorphous forms]

[A] Crystalline Form.

1. Diamond :

Diamond occurs naturally in Brazil, South Africa, Ural mountains, Australia and in Goleconda in India.

Two types of natural diamond are found in nature—(i) a colourless and glistening variety and (ii) a black opaque variety known as *carbonado.* It is due to its beauty, rarety and lustre, diamond is prized as a unique gem. The weight of diamond is expressed in *carats* (1 carat = 0·2 g). The famous *'Kohinoor'* was found in the sands of the Krishna river in South India, which adores the crown of England.

• Extraction of diamond from the natural sources :

Diamonds are found in the alluvial diposits mixed with rocks and gravels. Rocks and gravels rich in diamond are left exposed to open atmosphere when they are converted to powder. The larger crystals of diamond are first separated as far as possible by hand picking. After separating the larger crystals the powdered residue is mixed with water and the suspension is led over plane board coated with grease. Small particles of diamond being heavier than clay particles, adhere to the grease and clay particles pass on with water. The particles of diamond are then recovered from the board.

• Preparation of artificial diamond :

The first attempt to prepare artificial diamond was made by **Moissan** in 1893, A mixture of pure iron and sugar charcoal was taken in a graphite crucible and the mixture was heated in electric arc furnace to 3000°C. At this high temperature the mass in the crucible was melted and this molten iron dissolved a good amount of sugar charcoal. The crucible with its contents was then immersed in molten lead. Thus on rapid cooling the molten iron solidified producing a high pressure on the carbon. At this high pressure some part of the dissolved carbon crystallised out as small crystals of diamond. These crystals were separated from iron by dissolving iron in boiling hydrochloric acid.

• Properties of diamond :

[A] **Physical** : (i) Diamond is the *hardest substance* known.

(ii) In pure state it is colourless, transparent, lustrous and crystalline solid.

(iii) Of all the allotropes of carbon, diamond is the heaviest having the specific gravity 3·5.

(iv) Due to its high refractive index (2·42) it shines brightly in light.

(v) Diamond is *transparent to X-rays* and this property is utilised to distinguish a real diamond from the imitation diamond (made of glass) which is opaque to X-rays.

(vi) It is non conductor of heat and electricity.

[B] **Chemical** : (i) Diamond is chemically inert—*it is not attacked by acids or alkalis*. It is not attacked by chlorine or fused potassium chlorate.

(ii) Diamond is however *oxidised by oxygen* at 700°C producing *carbon di-oxide*.

$$\mathrm{C\ (diamond)} + O_2 = CO_2$$

(iii) It reacts with fused *sodium carbonate* to produce *sodium monoxide* and *carbon monoxide*.

$$Na_2CO_3 + \mathrm{C\ (diamond)} = Na_2O + 2CO \uparrow$$

(iv) It burns in *fluorine* to form *carbon tetra fluoride*. $C + 2F_2 = CF_4$

(v) It is oxidised by *chromic acid* (conc. $H_2SO_4 + K_2Cr_2O_7$) to produce CO_2.

(vi) Diamond dissolves in molten iron.

When diamond is heated with iron at 700°C—1000°C, the main product is iron carbide (Fe_3C) containing 6·6% of carbon. Formations of this compound goes to prove that diamond is nothing but an allotrope of carbon. It also proves that carbon is electronegative with respect to iron.

$$3Fe + C = Fe_3C.$$

• Uses of diamond : (i) Due to its bright lustre diamond is used as gem stone in jewellery. (ii) Due to its extreme hardness it is used for cutting glass and polishing hard surfaces. (iii) The black opaque diamond is known as carbonado and is used for drilling rocks.

• Structure of diamonds :

Explain why—(i) Diamond is the hardest substance known, (ii) Diamond does not conduct electricity, (iii) The melting point of diamond are very high.

The structure of diamond consists of a number of carbon atoms each of which is situated at the centre of a regular tetrahedron, surrounded by four other carbon atoms. These four carbon atoms are situated at the four corners of the tetrahedron. As a result, the bond angle C—C—C becomes 109°28′. Thus each carbon atom is strongly bonded to its four neighbours by strong covalent bonds resulted by sp^3 hybridisation. Thus all the carbon atoms are joined together covalently by strong sigma (σ) bonds, the C—C bond distance being 1·53Å. Such structure extends throughout the entire crystal in three diamensions and each crystal is regarded as giant molecule. This type of molecule is called *macro molecule*. Due to the extremely high strength of the covalent bonds holding numerous carbon atoms together, *diamond is very hard and has high density*.

As all the available electrons of the carbon atoms are completely paired up in forming the sigma bonds between the carbon atoms, no free electrons are left in the system for conducting electricity. This is why diamond is non-conductor of electricity.

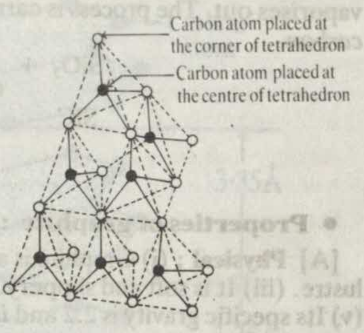

Carbon atom placed at the corner of tetrahedron
Carbon atom placed at the centre of tetrahedron

Fig 4.1 : Crystalline structure of diamond

The forces acting between the covalently linked carbon atoms in diamond are very strong and consequently a large amount of heat energy is needed to break so many covalent bonds in the crystal. So a large amount of heat energy is needed to melt it. This explains the high melting point of diamond.

2. Graphite :

Graphite is found in Sri Lanka, Italy, Siberia, California and in small quantities at Rajasthan, Orissa and Kerala in India.

- **Artificial preparation of graphite (Acheson's process) :**

In order to compensate the need of graphite, it is now manufactured artificially by **Acheson's process.**

An intimate mixture of *sand* (SiO_2) and *anthracite coke* is taken in a rectangular *electro-thermal furnace* made of fire bricks. The mixture is covered with a layer of sand. Two carbon electrodes, connected together by a central core of carbon rod, are placed in the mixture. The electric current is passed through the carbon rods when a high temperature is produced. The mixture of coke and sand is thus heated strongly to a temperature of 3500°C for 30 hours.

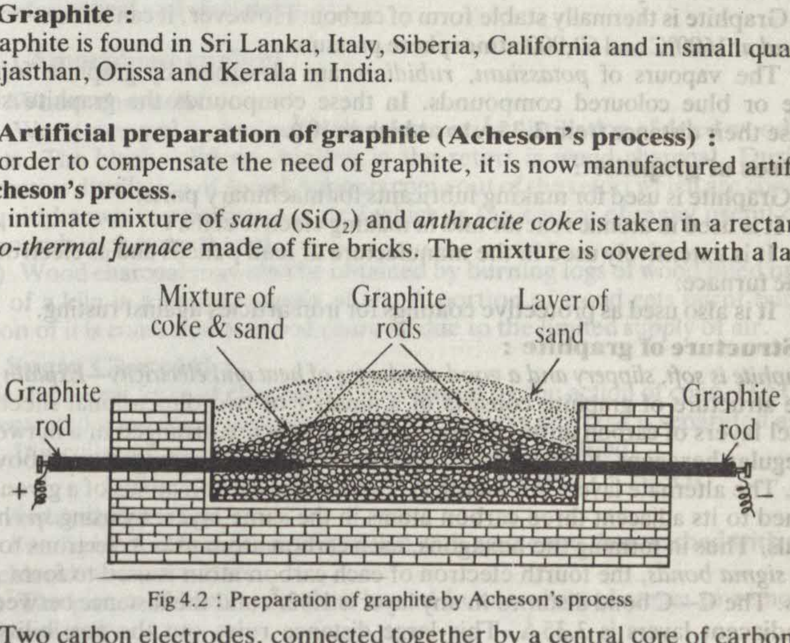


Fig 4.2 : Preparation of graphite by Acheson's process

Reaction : At this high temperature in the first step, carbon reacts with silica to produce *silicon carbide.*

In the next step, the silicon carbide thus produced, decomposes at a very high temperature into *graphite* and *silicon.* The silicon being more volatile than carbon vaporises out. The process is carried out *in absence of air to prevent the oxidation of carbon.*

$$SiO_2 + \underset{\text{Coke}}{3C} = SiC + 2CO\uparrow$$

$$SiC = \underset{\text{Graphite}}{C} + Si\uparrow$$

- **Properties of graphite :**

[A] **Physical :** (i) Graphite is a dark grey crystalline substance. (ii) It has metallic lustre. (iii) It is soft and slippery. (iv) It is a good conductor of heat and electricity. (v) Its specific gravity is 2.2 and *it marks paper.*

[B] **Chemical :**

(i) At 700°C graphite burns in oxygen and is oxidised to *carbon di-oxide.*

$$C\,(\text{graphite}) + O_2 = CO_2$$

(ii) It burns in *fluorine* at 500°C producing *carbon tetra fluoride.*

$$C + 2F_2 = CF_4$$

(iii) In presence of *conc.* HNO_3 *and* H_2SO_4 graphite reacts with *potassium chlorate* producing *graphitic acid.*

(iv) Graphite is not attacked by dilute acids or fused alkalis. It is oxidised by *chromic acid to* CO_2.

(v) Graphite is thermally stable form of carbon. However, it can be *converted to diamond at* 1600°C and 60,000 atmosphere pressure.

(vi) The vapours of *potassium, rubidium* are absorbed by graphite forming bronze or blue coloured compounds. In these compounds the graphite sheets increase their distance from 3.35Å to as high as 10Å.

- **Uses of graphite :**

(i) Graphite is used for making lubricants for machinary parts.

(ii) It is used in atomic reactor and in making electric cells.

(iii) It is extensively used in the manufacture of lead pencils and as electrodes in electric furnace.

(iv) It is also used as protective coatings for iron articles against rusting.

- **Structure of graphite :**

Graphite is soft, slippery and a good conductor of heat and electricity—Explain why.

The structure of graphite consists of a number of two dimensional sheets like parallel layers of carbon atoms. These carbon atoms are arranged in a network of flat regular hexagons. Such layers of carbon skeleton are arranged one above the other. The alternate layers are identical. Each of the carbon atoms of a given layer is joined to its adjacent three carbon atoms in the same layer, by using sp^2 hybrid orbitals. Thus in forming the hexagons, each carbon atom uses 3 electrons to form three *sigma bonds,* the fourth electron of each carbon atom is used to form *Pi* (π) *bonds.* The C—C bond distance in any layer is 1.42Å and the distance between the two adjacent layers is 3.35Å. This large distance rules out the possibility of a covalent bond between the carbon atoms in different layers. These layers are loosely linked together by *weak Vander waal's forces.* **The low density and softness of graphite is due to the wide separation of the sheet like carbon layers.**

Since the different layers are loosely linked together, they can easily slide over each other and as a result **graphite is slippery and possesses lubricating property in** contrast to the abrasive property of diamond. **As the Pi (π) electrons of carbon atoms are mobile and are free to move through the graphite crystal, graphite is a good conductor of heat and electricity.**

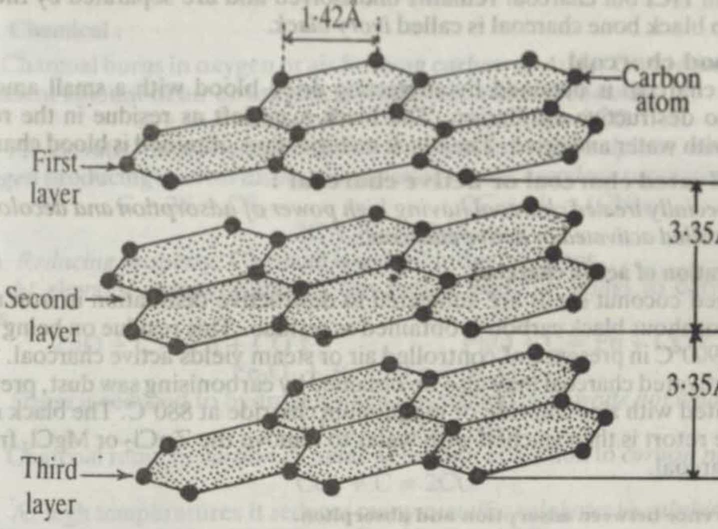


Fig 4.3 : Crystalline structure of graphite

[B] Amorphous carbon :

1. **Wood charcoal :**

(i) Wood charcoal is obtained by the destructive distillation of dried wood in iron retorts. The black solid residue left in the retort is wood charcoal. During the destructive distillation of wood, vapours come out of the retort which are condensed to liquid known as *pyroligneous acid* which is the source of many useful organic compounds such as methanol.

(ii) Wood charcoal may also be obtained by burning logs of wood piled up in the form of a kiln in a limited supply of air. A portion of wood gets burnt but major portion of it is converted to wood charcoal due to the limited supply of air.

2. **Sugar Charcoal :**

It is the purest form of charcoal. It is obtained by the action of conc. H_2SO_4 on a concentrated solution of sugar (sucrose) when sugar charcoal is separated as black mass. It is collected and washed with water, filtered and dried.

$$C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow 12C\downarrow + 11H_2O + H_2SO_4$$

3. **Animal charcoal :**

(i) Small pieces of bones are first boiled with water and then washed with carbon tetrachloride to remove fats.

(ii) The pieces of bones are then heated in superheated steam to remove the gelatinous matter.

(iii) The dried bones are then subjected to destructive distillation in iron retorts. The volatile matters are distilled away and bone charcoal is obtained in the retort as black residue.

(iv) It contains 10% carbon and 90% calcium phosphate and calcium carbonate. The impurities are removed by treating it with dilute HCl. $CaCO_3$ and $Ca_3(PO_4)_2$ dissolve in HCl but charcoal remains undissolved and are separated by filtration. This deep black bone charcoal is called *ivory black*.

4. **Blood charcoal :**

Blood charcoal is obtained by subjecting dried blood with a small amount of potash, to destructive distillation. The black mass left as residue in the retort is washed with water and dried. The black material thus obtained is blood charcoal.

- **Activated charcoal or active charcoal :**

Any specially treated charcoal having high power of adsorption and decolourising power is called activated or active charcoal.

Preparation of active charcoal.

(i) Dried coconut shells are subjected to destructive distillation in iron retorts, when amorphous black carbon is obtained as residue. This residue on being heated at 800°—900°C in presence of controlled air or steam yields active charcoal.

(ii) Activated charcoal may also be obtained by carbonising saw dust, previously impregnated with zinc chloride or magnesium chloride at 880°C. The black residue left in the retort is then leached with water to remove the $ZnCl_2$ or $MgCl_2$ from the active charcoal.

- **Difference between adsorption and absorpiton.**

The property, by virtue of which a substance can take up a particular substance and retain the same on its surface is called adsorption.

As a result the concentration of the particular substance on the surface of a solid or liquid becomes greater than it is present in its bulk. Adsorption is purely a surface phenomenon. The substance which takes up the particular substance or its surface, is called *adsorbant* and the substance which accumulates on the surface of on adsorbant is called *adsorbate*.

In the process of absorption a substance is uniformly distributed through out the body of a solid or liquid.

- **Properties of active charcoal :**

(i) Active charcoal has the power to adsorb colouring matters from the coloured solutions.

(ii) Active charcoal is a good adsorbent for gases than ordinary charcoal.

(iii) It has the power to adsorb taste of a substance.

(iv) Active charcoal acts as catalyst. It can accelerate many chemical reactions e.g.,

(a) Sulphur di-oxide combines with chlorine in presence of active charcoal which acts as catalyst.

$$SO_2 + Cl_2 \xrightarrow[\text{charcoal}]{\text{active}} SO_2Cl_2$$

(b) Chlorine combines with carbon monoxide in presence of active charcoal to form carbonyl chloride.

$$CO + Cl_2 \xrightarrow[\text{charcoal}]{\text{active}} COCl_2$$

- **Properties of charcoal :**

[A] **Physical :**

(i) Charcoal is black, porous and soft solid having a specific gravity of 1.4 to 1.9.

(ii) It is non conductor of heat and electricity.

(iii) Charcoal though heavier than water, is found to float on water, as much air is present in its pores.

(iv) Charcoal has the power to adsorb gases.

[B] **Chemical :**

(i) Charcoal burns in oxygen or air forming *carbon di-oxide.* On combustion with insufficient amount of air or oxygen, it produces carbon monoxide.

$$C + O_2 = CO_2 \qquad 2C + O_2 = 2CO$$

(ii) At elevated temperatures charcoal combines with *sulphur, nitrogen* and *hydrogen* producing *carbon disulphide, cyanogen* and *acetylene* respectively.

$$C + 2S = CS_2, \qquad 2C + N_2 = (CN)_2$$

$$2C + H_2 = C_2H_2$$

(iii) *Reducing property.* Charcoal is a good reducing agent.

(a) At elevated temperatures, it can reduce *metallic oxides* to corresponding metals.

$$ZnO + C = Zn + CO\uparrow, \qquad PbO + C = Pb + CO\uparrow$$

$$Fe_2O_3 + 3C = 2Fe + 3CO\uparrow$$

(b) *Steam* is reduced to hydrogen when it is passed over *white hot charcoal.*

$$C + H_2O = CO + H_2$$

(c) Charcoal reduces *carbon di-oxide* at red hot condition to *carbon monoxide.*

$$CO_2 + C = 2CO$$

(d) At high temperatures it reduces many *metallic sulphates* to *sulphides.*

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

(e) *Burning charcoal* reduces *conc. HNO_3* and *conc. H_2SO_4* to *nitrogen di-oxide* and *sulphur di-oxide* respectively.

$$C + 4HNO_3 = CO_2 + 4NO_2 + 2H_2O$$

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$

Charcoal is not attacked by dilute or conc. HCl.

(iv) *Formation of carbides :*

(a) At high temperature charcoal combines with *iron, aluminium* and *calcium* producing their respective *carbides.*

$$3Fe + C = Fe_3C, \qquad 4Al + 3C = Al_4C_3$$

$$Ca + 2C = CaC_2$$

(b) *Silicon* reacts with charcoal at 2000°C to form *silicon carbide.*

$$SiO_2 + 3C = SiC + 2CO$$

- **Uses of charcoal :**

(i) Wood charcoal is used as reducing agent and in detecting metallic radicals by charcoal test.

(ii) Ivory black is used as pigment. Blood charcoal is used as medicine to remove gas from the stomach and to eliminate some poisons.

(iii) It is used as gas adsorbing agent and in the preparation of gas mask.

(iv) It is extensively used in the preparation of gun powder. Animal charcoal is used in decolourising and purifying sugar.

4. Lamp black.

It is the purest form of amorphous carbon. It is prepared by burning *petrolium, benzene, terpentine, kerosene* and the other substances rich in carbon, in limited supply of air. As a result of their burning, thick smokes are produced which are led into chambers where wet blankets are kept suspended. Fine particles of carbon deposit on the blankets as soot.

- **Properties :** It is amorphous powder having specific gravity 1.7—1.8. It is no conductor of heat and electricity.

- **Uses :** It is extensively used in the manufacture of printers ink, black paints and shoe polish.

5. Coke.

Coke is prepared by the destructive distillation of coal. It is obtained as a black solid residue left in the retorts after the destructive distillation.

The carbonisation of coal when carried out at 600°C—700°C, soft coke is obtained. By high temperature carbonisation (1000°C—1200°C) hard coke is produced.

- **Properties :** Coke is porous black amorphous solid. It is bad conductor of heat and electricity. (i) It reacts with silica and quicklime to produce *silicon carbide (carborundum)* and *calcium carbide* respectively. When air is passed through white hot coke *producer gas* is obtained.

$$2C + (N_2 + O_2)\ (\text{air}) = 2CO + N_2$$

(ii) It reacts with steam in white hot condition to produce *water gas.*

$$C + H_2O = CO + H_2\ (\text{water gas})$$

(iii) At high temperature, it reduces many metallic oxides to produce their respective metals.

$$Fe_2O_3 + 3C = 2Fe + 3CO \uparrow$$
$$CuO + C = Cu + CO \uparrow$$

- **Uses :** Coke is largely used as reducing agent in the extraction of metals.

6. Gas carbon.

Gas carbon is obtained as hard dense black deposit in the inner wall of the retorts during the destructive distillation of coal.

It is chemically inert and a good conductor of heat and electricity.

- **Uses :** It is largely used in making electrodes of electric furnace and of galvanic cells. It is also used in the preparation of arc lamps.

- **Comparison of the properties of different allotropes of carbon :**

Properties	Diamond	Graphite	Charcoal	Lampblack	Gas carbon
(1) Colour	Colourless crystalline having bright lustre	Greyish black crystalline having metallic lustre	Black amorphous and opaque	Black amorphous and opaque	Black amorphous and opaque
(2) Specific gravity	3·5	2·25	1·4—1·9	1·7—1·8	~2·0
(3) Porosity	not porous	not porous	porous	not porous	not porous
(4) Conductivity	non conductor of heat and electricity	conductor of heat and electricity	non-conductor	non-conductor	good conductor
(5) Carbon contents	100%	95—97%	60—70%	90%	95—97%
(6) Adsorption power	Has no adsorption power	Has no adsorption power	Wood charcoal has adsorption power	Has no adsorption power	Has no adsorption power

Properties	Diamond	Graphite	Charcoal	Lampblack	Gas carbon
(7) **Hardness**	Extremely hard	Soft and slippery	Soft and porous	Soft and powder	Very hard
(8) **Combustibility**	800°C—900°C	700°C	Combustible at ordinary temperatures	Combustible at ordinary temperatures	at 700°C

• To prove that all the allotropic modifications of carbon contain the same element.

When a fixed amount of each of the different allotropes of carbon in pure state is separately burnt in pure and dry oxygen, it is completely oxidised to give carbon di-oxide only. It has been found that the same amount of any allotrope of carbon produces exactly the same weight of carbon di-oxide. This proves that different allotropes of carbon are nothing but carbon.

A fixed amount of each of the different allotropes of carbon in pure state is accurately weighed and taken in a completely dried porcelain boat. The boat along with the sample is then introduced into a combustion tube. The other end of the combustion tube is packed with pure and dry cupric oxide. A stream of pure O_2 is passed through the end of the combustion tube near the boat. When all the air inside the combustion tube is expelled, a previously weighed potash bulb containing strong caustic potash solution is connected to the exit end of the combustion tube. The other end of the potash bulb is further attached to a guard tube containing fused $CaCl_2$ and sodalime to prevent the entry of CO_2 and moisture of air into the potash bulb.

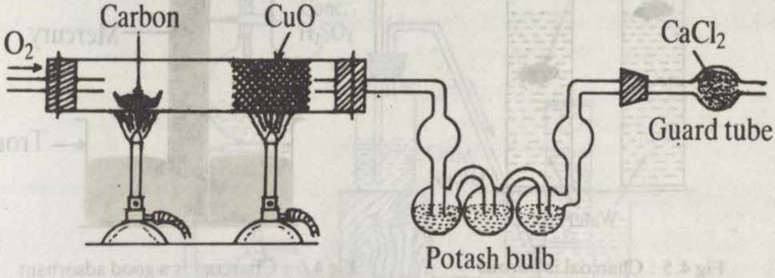


Fig 4.4 : Allotropic modifications of carbon contains the same element

The cupric oxide layer and the porcelain boat is strongly heated and the flow of O_2 into the tube is continued. The carbon in the boat is completely burnt in O_2 to produce CO_2 and some CO. The CO thus formed is oxidised to CO_2 while passing over heated CuO.

$$C + O_2 = CO_2$$
$$2C + O_2 = 2CO$$
$$CuO + CO = Cu + CO_2$$

The produced CO_2 is absorbed in the potash bulb. After the completion of the reaction the potash bulb is detached and weighed accurately. The increase in weight of the potash bulb gives the weight of the CO_2 produced on complete combustion of the known weight of the sample of carbon. It has been found that the same weight of different allotropes of carbon produces the same amount of carbon di-oxide. Thus it is proved that different allotropes of carbon contains the same element i.e., carbon.

- **To prove the porosity of charcoal :**

The specific gravity of charcoal is 1.4 to 1.9. It is heavier than water and consequently it should sink in water, but practically it floats on water. A piece of charcoal is taken in a gas jar containing water. It is observed that it floats on water. The mouth of the jar is closed with a rubber cork fitted with a glsss tube. The tube is connected with an air pump. Now the air inside the gas jar is drawn out by means of the pump. It is observed that as the pump works the air escapes from the pores of the charcoal producing small bubbles on its surface and gradually it begins to sink in water. Thus it is proved that charcoal is porous and the numerous pores in charcoal are filled with air which is expelled as bubbles on evacuation of the jar.

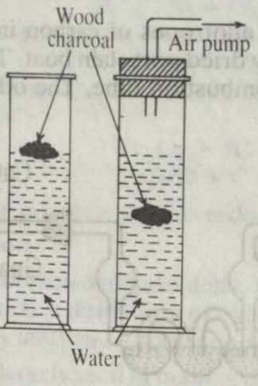


Fig 4.5 : Charcoal is porous

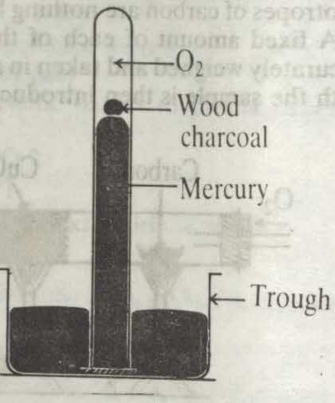


Fig 4.6 : Charcoal is a good adsorbant

- **To prove that charcoal is a good adsorbant :**

A glass tube closed at one end is filled with oxygen gas and is inverted over mercury in a trough. A piece of wood charcoal is heated to expel the air inside its pores and is then introduced into the glass tube. It is found that the mercury column inside the glass tube gradually rises up and finally fills the tube. If the same experiment is repeated with other gases separately the result is the same.

This is due to the fact that oxygen inside the tube is adsorbed by the piece of charcoal producing thereby a vacuum inside the tube which causes the mercury column to rise up to fill the vacuum.

• OXIDES OF CARBON •

Carbon forms two principal oxides—

(i) *Carbon di-oxide (CO_2)* (ii) *Carbon monoxide* (CO) : a less important oxide is *carbon suboxide* (C_3O_2). All the oxides of carbon are gases.

4.5. Carbon monoxide.

Carbon monoxide was first discovered by Lassone in 1766 by heating charcoal with zinc oxide. Carbon monoxide seldom occurs free in nature. It is found in coal gas and in the exhaust gases of motor engine.

• Laboratory method of preparation.

[A] Principle :

Carbon monoxide is generally prepared in the laboratory by heating *formic acid* or *oxalic acid* with *concentrated sulphuric acid.* Concentrated H_2SO_4 dehydrates formic acid or oxalic acid yielding carbon monoxide.

$$HCOOH + H_2SO_4 = CO\uparrow \quad + [H_2O + H_2SO_4]$$

$$\begin{array}{l}COOH\\ \mid\\ COOH\end{array} + H_2SO_4 = CO + CO_2 + [H_2O + H_2SO_4]$$

[B] **Procedure :** Concentrated sulphuric acid is taken in a round bottomed flask fitted with a dropping funnel and a delivery tube. The flask is clamped to a stand and kept on a wire gauze on a tripod stand. The free end of the delivery tube dips in conc. NaOH solution in a gas washer. The gas washer is fitted with another delivery tube the free end of which is dipped in water in a trough. A gas jar completely filled with water is kept inverted over the end of the delivery tube. The flask is now heated to 100°C and formic acid is allowed to fall dropwise on the hot conc. H_2SO_4 from the dropping funnel. As a result of dehydration of formic acid carbon monoxide evolves which passes through the caustic soda solution and is collected in the gas jar by the displacement of water.

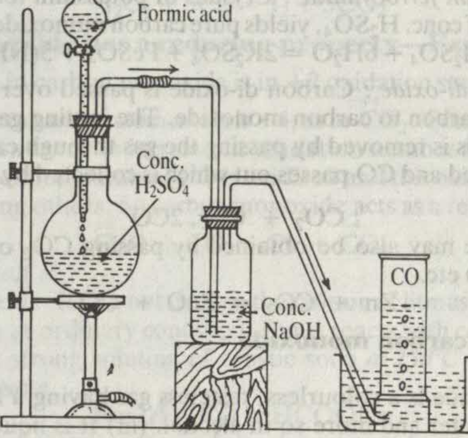


Fig 4.7 : Laboratory method of preparation of carbon monoxide

[C] **Purification :** The carbon monoxide thus produced is dried by passing it through P_2O_5 and is collected over mercury.

Carbon monoxide is not dried by conc. H_2SO_4, because conc. H_2SO_4 being an oxidising agent, small portion of CO is oxidised by conc. H_2SO_4 to CO_2.

$$H_2SO_4 = H_2O + SO_2 + O$$

$$CO + O = CO_2$$

• Carbon monoxide from oxalic acid :

(1) Crystals of oxalic acid are taken in a round bottomed flask fitted with a dropping funnel and a delivery tube. The end of the delivery tube is dipped in a gas-washer containing conc. NaOH solution.

The gas washer is fitted with another delivery tube. The free end of which is kept immersed in water in a trough. Conc. H_2SO_4 is allowed to fall dropwise on oxalic acid and the mixture is heated to 60°C. As a result of dehydration of oxalic acid equal volumes of CO and CO_2 are produced which pass through the NaOH solution in a gas washer. Here CO_2 is absorbed and carbon monoxide passes out which is collected in a gas jar by the displacement of water.

(2) *From sodium formate :* When dry sodium formate is heated slowly with conc. H_2SO_4 carbon monoxide is evolved. The reaction takes place in two steps. At first formic acid is produced by the action of sodium formate with conc. H_2SO_4 In the second step the produced formic acid is dehydrated by conc. H_2SO_4 yielding CO.

$$\begin{array}{l} HCOONa + H_2SO_4 = NaHSO_4 + HCOOH \\ HCOOH + H_2SO_4 = CO\uparrow + H_2O + H_2SO_4 \\ \hline HCOONa + H_2SO_4 = NaHSO_4 + H_2O + CO \end{array}$$

(3) *From potassium ferrocyanide :* Crystals of potassium ferrocyanide on being heated with excess of conc. H_2SO_4, yields pure carbon monoxide in the laboratory.

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO\uparrow$$

(4) *From carbon di-oxide :* Carbon di-oxide is passed over red hot coke when CO_2 is reduced by carbon to carbon monoxide. The issuing gas may contain some unreduced CO_2. This is removed by passing the gas through caustic soda solution, when CO_2 is absorbed and CO passes out which is collected by the displacement of water.

$$CO_2 + C = 2CO$$

Carbon monoxide may also be obtained by passing CO_2 over strongly heated metals like *zinc*, *iron* etc.

$$Zn + CO_2 = ZnO + CO$$

- **Properties of carbon monoxide :**

[A] **Physical :**

(i) Carbon monoxide is a colourless, tasteless gas having a faint odour. (ii) It is slightly soluble in water and more so in alcohol. (iii) It is liquefied to a colourless liquid at −191°C at ordinary pressure. (iv) It is highly poisonous.

The fatal action of carbon monoxide is because of the fact that it combines with haemoglobin of blood producing carboxy haemoglobin. Thus haemoglobin—the oxygen carrier in living organism is destroyed. Such blood contains carboxy haemoglobin in place of haemoglobin and as a result it can not take part in the normal oxygen exchange process. As a result the oxygen transportation is disturbed and so the tissues do not get necessary oxygen and ultimately death occurs. This explains why people sleeping in a closed room with charcoal fire burning inside, dies. A victim of CO when unconscious, should be taken in an open place and artificial respiration with *carbogen* (a mixture of oxygen and 5–10% CO_2) should be given.

[There is a similarity in the molecular structure of N_2 and CO. The number of valence electrons in both the molecule are the same.

$$:N\equiv N: \qquad :C\equiv O:$$

Consequently both N_2 and CO exhibit similar physical properties. Thus the vapour density, solubility, boiling point melting point etc., of these two gases are very similar.]

[B] **Chemical :**

(i) *Carbon monoxide is combustible but not a supporter* of combustion. It burns in air or oxygen *producing a blue flame* with the formation of *carbon di-oxide*. This reaction is exothermic.

$$2CO + O_2 = 2CO_2 + 135{\cdot}2 \text{ kcal}$$

(2) *Reducing property :*

(a) Carbon monoxide acts as a reducing agent at high temperatures. At red hot condition metallic oxides are reduced to metals. Thus when CO is passed over strongly heated *cupric oxide, ferric oxide, lead oxide, zinc oxide etc.*, these are reduced to the *corresponding metals.*

$$\begin{aligned} CuO &+ CO &&= Cu &&+ CO_2 \\ Fe_2O_3 &+ 2CO &&= 2Fe &&+ 3CO_2 \\ ZnO &+ CO &&= Zn &&+ CO_2 \end{aligned}$$

(b) In presence of a mixture of *ferric oxide* (Fe_2O_3) and *chromic oxide* (Cr_2O_3) as catalyst, carbon monoxide *reduces steam* to *hydrogen* at 550°C.

$$\overset{+2}{C}O + \overset{+1}{H_2}O = \overset{+4}{C}O_2 + \overset{0}{H_2}$$

(c) *At 90°C, I_2O_5 is reduced* by carbon monoxide to produce the violet vapours of *free iodine.*

$$I_2O_5 + 5CO = I_2 + 5CO_2$$

- **Carbon monoxide has a reducing property—Explain why.**

The carbon atom in carbon monoxide is in +2 oxidation state $[\overset{+2}{C}O]$. The highest oxidation state that can carbon atom attain is +4, as in $\overset{+4}{C}O_2$. Consequently the carbon atom of CO has a tendency to increase its oxidation number from +2 to +4. Thus by increasing its oxidation number, CO is oxidised and this oxidation is brought out at the cost of reducing others. So carbon monoxide acts as a reducing agent.

$$\overset{+2}{Cu}O + \overset{+2}{C}O = \overset{0}{Cu} + \overset{+4}{C}O_2$$

(3) *Action on alkali :*

CO is a neutral oxide. It can not change the colour of litmus. So it does not react with bases or alkalis at ordinary condition. But it reacts with *caustic soda* when CO is passed through a strong solution of caustic soda *at 150°C under high pressure, yielding sodium formate.*

$$NaOH + CO = HCOONa$$

(4) *Formation of addition compounds (carbonyls) :* Since all the valencies of carbon in carbon monoxide are not satisfied, it thus behave as an unsaturated compound and forms addition products with a number of elements and compounds.

(i) CO directly combines with *chlorine in presence of sunlight* or *charcoal* catalyst yielding *carbonyl chloride* or *phosgene*. It is highly poisonous.

$$CO + Cl_2 = COCl_2$$

(ii) *It combines directly with sulphur* when a mixture of sulphur vapour and CO is passed through a heated tube with the formation of *carbonyl sulphide.*

$$CO + S = COS$$

(iii) Carbon monoxide combines with many transitional metals like *iron, cobalt, nickel* forming the corresponding *carbonyls.*

$$Ni + 4CO = \xrightarrow{50°C—80°C} Ni(CO)_4, \quad Fe + 5CO \xrightarrow{180°} Fe(CO)_5$$

(5) *Absorbant of CO :* Carbon monoxide is completely absorbed by a solution of *cuprous chloride in concentrated hydrochloric acid* or in *ammonium hydroxide.* Carbon monoxide forms a *white crystalline addition compound* with the reagent.

$$Cu_2Cl_2 + 2CO + 4H_2O = 2[CuCl, CO, 2H_2O]$$

(6) At 300°C in presence of ZnO and Cr_2O_3 as catalyst, CO react with H_2 to form *methyl alcohol.*

$$CO + 2H_2 = CH_3OH$$

• Tests of carbon monoxide :

(i) Carbon monoxide burns with a pale blue flame when ignited.

[Both H_2 and CO burns with a pale blue flame when ignited. Hydrogen burn in air or oxygen to form steam which turns anhydrous white $CuSO_4$ blue. Carbon monoxide burns in air or oxygen to form CO_2 which turns lime water milky.]

(ii) CO turns *ammoniacal $AgNO_3$ solution brown.*

(iii) CO is completely absorbed by *ammoniacal cuprous chloride* solution.

(iv) A filter paper soaked with a solution of *platinum or palladium chloride,* when comes in contact with CO, turns *pink* or *green* or *black* due to the reduction of the salt.

$$PdCl_2 + H_2O + CO = Pd\downarrow + CO_2 + 2HCl$$

• Uses of CO :

(i) CO is used in the *extraction of nickel* and *as a reducing agent* in the extraction of metals.

(ii) It is used *as a fuel* in the form of *producer gas, water gas.*

(iii) It is extensively used in the synthetic preparation of *methanol, methane* and *artificial petrol.*

• Structure of carbon monoxide :

The electronic structure of carbon monoxide may be expressed as—

$$:\mathrm{C}\,\underset{\times}{\vdots}\,\underset{\times}{\overset{\times}{\times}}\,\mathrm{O}\,\overset{\times}{\times} \qquad \text{or} \qquad :\mathrm{C}\underset{\leftarrow}{\equiv}\mathrm{O}\,\overset{\times}{\times}$$

The presence of a triple bond in C and O atom in CO is proved by the following facts—(i) The C–O bond length in CO is 1·13Å which corresponds to that of a carbon-oxygen triple bond.

(ii) Though there is a large difference in the electro negativities of C and O, it is found that CO molecule exhibits only a small dipole moment. This is due to the shift of electron pair from oxygen atom to carbon atom which compensates the difference in electro-negative values.

(iii) Due to the presence of electron pair in carbon monoxide, it acts a Lewis base and can form a co-ordinate bond with some metals which are known as carbonyls.

$$[\mathrm{M}\leftarrow\mathrm{C}\overset{\leftarrow}{\equiv}\mathrm{O}] \qquad \mathrm{M} = \mathrm{Fe, Ni, Cr}\ \text{etc.}$$

• To prove that carbon monoxide contains carbon.

Pure and dry carbon monoxide is passed over red hot cupric oxide in a combustion tube. The gas coming out of the combustion tube through the outlet tube, is collected in a gas jar. A piece of burning magnesium ribbon is then introduced into the gas jar when it continues to burn in it. After the completion of the reaction, the residue obtained is treated with dil. HCl when black particles are found to float on the solution inside the jar. The black particles are collected after filtration and dried and then burnt in oxygen when a colourless and odourless gas is obtained. The gas thus obtained turns lime water milky. This proves that the gas is CO_2 which is formed by the combustion of the black particles with oxygen. So the black particles are nothing but carbon. This carbon has come from carbon monoxide.

$$CuO + CO = Cu + CO_2$$

$$CO_2 + 2Mg = 2MgO + \underset{\substack{\text{Black}\\ \text{particles}}}{C\downarrow}$$

$$C + O_2 = CO_2 \ ; \qquad Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$

- **How to convert a mixture of CO and CO_2 (i) completely into CO_2 or (ii) completely into CO :**

(i) A mixture of CO and CO_2 is passed over red hot cupric oxide in a combustion tube. CO_2 remains unchanged but CO reduces CuO to metallic Cu and itself being oxidised to CO_2. As a result the gas comming out of the combustion tube is only CO_2. Thus the mixture of CO and CO_2 is converted completely into CO_2.

$$CO + CuO = CO_2 \uparrow + Cu$$

(ii) The mixture of CO and CO_2 is passed over white hot coke when CO_2 is reduced by coke to form CO and CO remains unchanged.

$$CO_2 + C = 2CO.$$

- **To prove that carbon monoxide is a reducing agent.**

A small amount of black cupric oxide is taken in a combustion tube fitted with an inlet tube at one end and an outlet tube at the other. The end of the outlet tube is kept immersed in lime water in a bottle. The cupric oxide is strongly heated and a slow stream of dry CO is passed over the heated CuO. It is observed that the black CuO gradually turns red. A colourless gas is found to come out through the outlet tube which passes through the lime water turning it milky. The unreacted carbon monoxide burns at the mouth of the outlet tube, which comes out from the bottle. After the completion of the reaction a red residue is obtained in the combustion tube. The red residue is dissolved in HNO_3 when a blue solution is obtained. The blue solution on treatment with excess of NH_4OH yields a deep blue solution of cupro ammonium salt. This proves that the red residue is nothing but metallic copper which is produced by the reduction of black CuO. The gas coming out of the combustion tube turns lime-water milky. This proves that the gas is CO_2 which is produced by the oxidation of carbon monoxide.

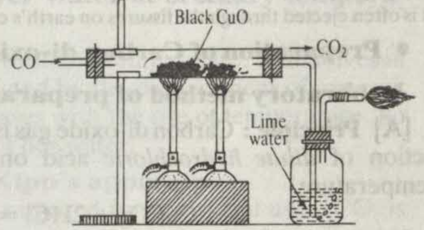


Fig 4.8 : CO is a reducing agent

$$CuO + CO = Cu + CO_2$$
$$Ca(OH)_2 + CO_2 = CaCO_3 \downarrow + H_2O.$$

- **Comparison of the properties of carbon monoxide and nitric oxide :**

Carbon monoxide	Nitric oxide
1. A colourless gas—insoluble in water.	1. A colourless gas insoluble in water.
2. A neutral oxide—cannot change the colour of litmus.	2. A neutral oxide—can not change the colour of litmus.
3. A combustible gas—burns with a pale blue flame in air or oxygen.	3. A non-combustible gas.
4. Reacts with oxygen when burnt in it to form CO_2 which is acidic oxide. $2CO + O_2 = 2CO_2$	4. Reacts with oxygen at ordinary temperature to form NO_2 which is an acidic oxide. $2NO + O_2 = 2NO_2$
5. CO combines with oxygen when burnt to form CO_2.	5. Nitric oxide combines with oxygen at ordinary temperature to form the brown fumes of nitrogen di-oxide.
6. At 200°C, CO reacts with NaOH under high high pressure to form sodium formate. $NaOH + CO = HCOONa$	6. Nitric oxide does not react with NaOH under any condition.

Carbon monoxide	Nitric oxide
7. CO can form addition compound e.g., $COCl_2$ $CO + Cl_2 = COCl_2$	7. NO can form addition compound e.g., NOCl.
8. CO is absorbed by ammoniacal cuprous chloride solution forming an additive compound. $2[CuCl, CO\ 2H_2O]$	8. NO is absorbed in ferrous sulphate solution forming an additive compound. $Fe[(NO)(H_2O)_5]SO_4$
9. CO is highly poisonous.	9. NO is a poisonous gas.
10. CO has reducing property.	10. NO has both the oxidising and reducing property.

4.6. Carbon di-oxide.

In 1630 **Van Helmont** discovered carbon di-oxide by burning wood and other carbonacious substances. **Lavoisier** proved CO_2 to be acidic in nature and called it carbonic acid gas.

Carbon di-oxide occurs in air to the extent of about 0·04% by volume. It is produced by the combustion of carbonacious fuels, respiration of plants and animals and from the decomposition of organic matters. It is often ejected through the fissures on earth's crust in volcanic region.

• Preparation of Carbon di-oxide.

Laboratory method of preparation :

[A] **Principle :** Carbon di-oxide gas is generally prepared in the laboratory by the action of *dilute hydrochloric* acid on *marble (calcium carbonate)* at ordinary temperature.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

[B] **Procedure :** Small pieces of marble are taken in a woulfe's bottle fitted with a thistle funnel and a delivery tube. Water is added into the woulfe's bottle through the thistle funnel so that the marble pieces and the end of the thistle funnel are kept under water level. The end of the delivery tube is inserted into the gas jar. Now moderately strong hydrochloric acid is poured down the thistle funnel. As soon as the acid comes in contact with the marble, carbon di-oxide evolves producing effervescence. The evolved gas passes through the delivery tube and is collected in the gas jar *by the upward displacement of air.*

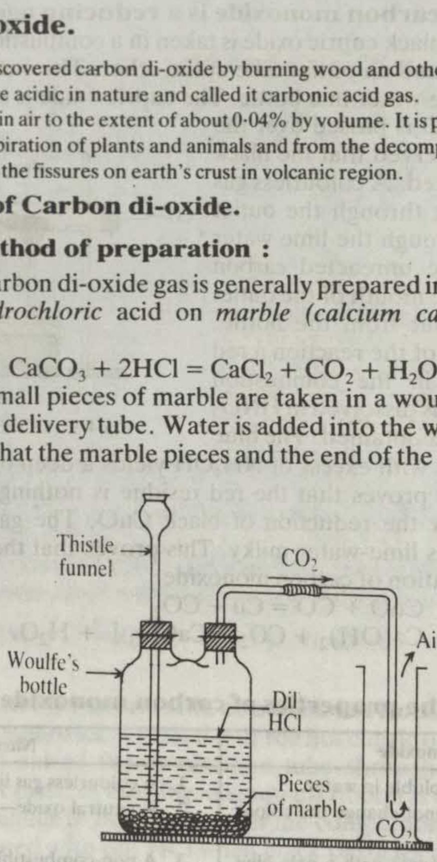


Fig 4.9 : Laboratory method of preparation of carbon di-oxide

[C] **Purification :** Carbon di-oxide thus prepared may contain some *HCl vapours* and *moisture.* The HCl vapour is removed by passing the gas through a solution of *sodium bicarbonate* and the moisture is removed by passing it through *conc.* H_2SO_4. The pure and dry CO_2 is collected over mercury.

• Dilute H_2SO_4 is not used in the preparation of CO_2 instead of dil. HCl—Explain why.

Any acid which is stronger than carbonic acid will liberate CO_2 from $CaCO_3$. But in the preparation of CO_2 by the action of acids on marble ($CaCO_3$) dil. H_2SO_4 can not be used, though H_2SO_4 is much stronger than carbonic acid. This is due to the fact that as soon as dil. H_2SO_4 comes in contact with marble, insoluble calcium sulphate is produced.

$$CaCO_3 + H_2SO_4 = CaSO_4\downarrow + CO_2 + H_2O$$

As calcium sulphate is insoluble in H_2SO_4, an insoluble layer of $CaSO_4$ is produced on the surface of the marble pieces. As a result dil. H_2SO_4 can not come in contact with the marble pieces and consequently the reaction stops.

If dilute HCl is used, $CaCl_2$ is formed by the action of HCl on marble which is soluble in water as well as in HCl. As a result dil. HCl reacts completely with marble with the evolution of CO_2.

• Carbon di-oxide is not collected over water at ordinary temperatures —Explain why.

Carbon di-oxide is fairly soluble in water at ordinary temperature. It dissolves in water forming carbonic acid. So it is not collected by the displacement of water at ordinary temperature. But its solubility decreases with the rise of temperature. So the gas may be collected by the displacement of hot water.

• Preparation of carbon di-oxide in Kipp's apparatus :

When a steady supply of carbon dioxide is required for occasional uses, CO_2 is prepared in Kipp's apparatus.

Small pieces of marble are taken in the central globe of the apparatus. The stop cock in the central globe is kept open and moderately strong HCl is poured down through the thistle funnel attached to the upper globe. As soon as the acid comes in contact with the marble pieces in the central globe, reaction takes place and CO_2 begins to evolve which passes out through the exit tube. After the removal of air inside the central globe, the stop cock is closed. As the evolved CO_2 can not come out, it exerts pressure on the acid and pushes it down into the lower globe. As a result the acid rises up and goes into the upper globe. Thus the marble pieces become out of contact with the acid and so the reaction stops.

Now on opening the stop cock the collected gas in the central globe passes out and the pressure on the acid is released. Then the acid from the upper globe enters the central globe again and reacts with the marble producing more CO_2 which is collected in the central globe when the stop cock is closed. This stored gas may be used again when needed.

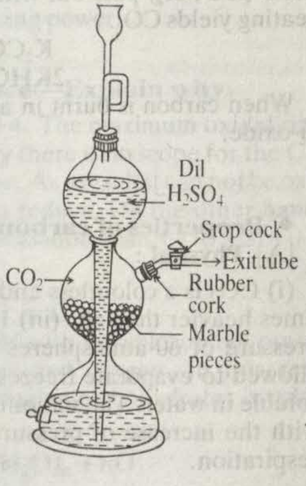


Fig 4.10 : Kipp's apparatus

• Other methods of preparation of CO_2 :

1. **By the action of metallic carbonates on dilute acids :**

Metallic carbonates react with dilute acids liberating carbon di-oxide.

$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2 + H_2O$$
$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$
$$CuCO_3 + 2HNO_3 = Cu(NO_3)_2 + CO_2 + H_2O$$

2. **By the thermal decomposition of carbonates and bicarbonates :**
With the exception of the carbonates of alkali metals, metallic carbonates at elevated temperature decompose to evolve carbon di-oxide and the corresponding oxides of the metals.

$$CaCO_3 = CaO + CO_2\uparrow \qquad MgCO_3 = MgO + CO_2\uparrow$$
$$PbCO_3 = PbO + CO_2\uparrow \qquad FeCO_3 = FeO + CO_2\uparrow$$

Sodium or potassium bicarbonate on being heated evolves CO_2.

$$2Na\,HCO_3 = Na_2CO_3 + CO_2 + H_2O$$

3. CO_2 is obtained *as by-product from the fermentation industry.* Thus in the manufacture of ethanol by the fermentation of glucose, carbon di-oxide is obtained as a by-product.

$$C_6H_{12}O_6 \xrightarrow[\text{Zymase}]{\text{Yeast } 30^\circ C} 2C_2H_5OH + 2CO_2\uparrow$$

4. **From water gas :**

Steam is passed over white hot coke when water gas is produced. It is a mixture of CO and H_2. In the next step excess of steam is mixed with water gas and the mixture is passed over *heated ferric oxide* and *chromic oxide* at 400°C which act as catalyst. *Carbon monoxide is oxidised by the steam to carbon di-oxide.*

$$C + H_2O = CO + H_2$$
$$\underset{\text{(Water gas)}}{CO + H_2} + \underset{\text{(Steam)}}{H_2O} = CO_2 + 2H_2$$

The mixture of CO_2 and H_2 thus obtained is then passed though potassium carbonate when CO_2 is absorbed by K_2CO_3 with the formation of $KHCO_3$ Other gases (CO, H_2) pass out without reacting with K_2CO_3. The produced $KHCO_3$ on heating yields CO_2.

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3$$
$$2KHCO_3 = K_2CO_3 + CO_2\uparrow + H_2O$$

When carbon is burnt in air, it combines directly with O_2 of air to form carbon di-oxide.

$$C + O_2 = CO_2$$

- **Properties of carbon di-oxide :**

[A] **Physical :**

(i) CO_2 is a colourless and odourless gas having a faint acidic taste. (ii) It is $1\frac{1}{2}$ times heavier than air. (iii) It can be liquefied to a colourless liquid by applying a pressure of 60 atmospheres at a temperature below 31°C. Liquid CO_2 on being allowed to evaporate freezes to a snow like solid called dry ice. (iv) CO_2 is fairly soluble in water. The solubility decreases with the rise of temperature but increases with the increase of pressure. (v) CO_2 is not poisonous but it does not support respiration.

[B] **Chemical :**

(1) **Combustibility :** CO_2 is neither combustible nor a supporter of combustion but burning *magnesium, sodium* and *potassium* continue to burn in it with the separation of *carbon.* Due to the tremendous heat produced during the burning of these metals, CO_2 decomposes to carbon and oxygen. The oxygen thus liberated helps the combustion of these metals and oxidises them.

$$2Mg + CO_2 = 2Mg + C$$
$$4K + 3CO_2 = 2K_2CO_3 + C$$

(2) **Acid property :**

(i) Carbon dioxide is an *acidic oxide* and its aqueous solution is acidic. It dissolves in water forming *carbonic acid* which is a weak dibasic acid.

$$CO_2 + H_2O = H_2CO_3$$

Carbonic acid turns blue litmus red but has no action on methyl orange.

(ii) *Action on bases and alkalis.* CO_2 being an acidic oxide, reacts with bases and alkalis producing *bicarbonates and carbonates.* With sodium hydroxide it produces sodium carbonate and sodium bicarbonate.

$$NaOH + CO_2 = NaHCO_3$$
$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

When CO_2 is passed through a clear lime water, the later turns milky due to the formation of insoluble calcium carbonate.

$$CO_2 + Ca(OH)_2 = CaCO_3\downarrow + H_2O$$

On passing excess of CO_2 in the milky lime water, the milkiness disappears due to the formation of clear solution of calcium bicarbonate which is soluble in water.

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

(3) **Action on metals—oxidising action of CO_2 :**

When CO_2 is passed over *red hot iron* or *zinc powder*, the metals are oxidised to their corresponding oxides.

$$2Fe + 3CO_2 = Fe_2O_3 + 3CO$$
$$Zn + CO_2 = ZnO + CO$$

Burning magnesium is oxidised by CO_2 to produce magnesium oxide and CO_2 is reduced to *carbon.*

$$2\overset{0}{Mg} + CO_2 = 2\overset{+2}{Mg}O + C$$

These reactions go to prove that CO_2 has oxidising power.

• CO_2 can oxidise only but can not reduce—Explain why.

The oxidation state of carbon atom in CO_2 is +4. The maximum oxidation state which can carbon atom attain is +4. Consequently there is no scope for the C-atom of CO_2 to increase its oxidation number any further. As a result it can not be oxidised by reducing the other substance. So CO_2 can not reduce. On the other hand, the carbon atom of CO_2 has the scope to decrease its oxidation from +4 to +2 or 0. Thus by reducing itself it can oxidise the others.

$$2\overset{0}{Mg} + \overset{+4}{C}O_2 = 2\overset{+2}{Mg}O + \overset{0}{C}$$

(4) In presence of sunlight and moisture, plants with the chlorophyll present in their leaves, can convert CO_2 to carbohydrates and oxygen. In this reaction chlorophyll acts as catalyst. Such process of producing carbohydrates by plants is known as *photo-synthesis.*

$$nCO_2 + nH_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} (CH_2O)_n + nO_2$$

(5) When a *mixture of CO_2 and NH_3 is passed* through *a suspension of gypsum in water,* insoluble $CaCO_3$ is precipitated with the formation of *ammonium sulphate.* By this proces, $(NH_4)_2SO_4$ is produced without the help of H_2SO_4.

$$2NH_3 + CO_2 + CaSO_4 + H_2O = CaCO_3 + (NH_4)_2SO_4$$

(6) *Action with ammonia.* At 200°C—210°C and under a pressure of 180 kilogram, CO_2 reacts with ammonia yielding *urea.*

$$CO_2 + 2NH_3 \rightleftharpoons \underset{\text{Ammonium carbonate}}{NH_4COONH_2} \rightleftharpoons \underset{\text{Urea}}{NH_2CONH_2} + H_2O$$

(7) When CO_2 is passed through a strong solution of sodium chloride (Brine), saturated with ammonia, sodium bi-carbonate is precipitated. CO_2 first reacts with ammonia producing NH_4HCO_3, which next reacts with NaCl to form $NaHCO_3$.

$$CO_2 + NH_4OH = NH_4HCO_3$$
$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

(8) *Carbon di-oxide is reduced to carbon monoxide* when CO_2 is passed over red hot coke.

$$CO_2 + C = 2CO.$$

(9) **Absorbant of CO_2**

CO_2 is absorbed by *strong caustic* soda or *caustic potash* solution forming carbonate or bicarbonate.

$$NaOH + CO_2 = NaHCO_3$$
$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

- **Tests for carbon di-oxide.**

(i) When carbon di-oxide is passed through clear lime water, the lime water turns milky due to the formation of insoluble *calcium carbonate.*

(ii) When excess of CO_2 is passed through it, the milkiness disappears and turns clear again due to the formation of soluble *calcium bicarbonate.*

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$
$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

When CO_2 is passed through an acidified solution of $K_2Cr_2O_7$, the orange colour of the solution does not turn green.

[SO_2 also turns lime water milky due to the formation of insoluble calcium sulphite and the milkiness disappears on passing excess of SO_2 due to the formation of soluble calcium bi-sulphite. But SO_2 differs from CO_2 in the fact that SO_2 can change the orange colour of acidified solution of $K_2Cr_2O_7$ to green but CO_2 can not change the orange colour of $K_2Cr_2O_7$ to green.]

- **Uses of CO_2 :**

(i) CO_2 is extensively used in the manufacture of sodium carbonate by *Solvey process, salicylic acid, urea* and *ammonium sulphate.* (ii) It is used as fire extinguisher. (iii) Solid CO_2 is known as dry ice. It is used as refrigerant for creating low temperature. (iv) It is used in the preparation aerated waters like soda water, lemonade etc.

- **Dry ice :**

When carbon di-oxide is subjected to a pressure of 60 atmospheres at ordinary temperature, it is liquefied to a colourless liquid. This liquid carbon di-oxide is kept in cylinders made of steel. The liquid CO_2 at 20°C and under a pressure of 70 atmospheres, is introduced into a chamber through a jet. Here rapid evaporation of liquid CO_2 takes place and the required amount of latent heat for its evaporation is supplied by the liquid CO_2 itself. As a result, the temperature of liquid CO_2 gradually falls down to 0°C. The liquid CO_2 at 0°C is then admitted to press chamber where further evaporation takes place and the colourless liquid CO_2 freezes like white snow. This is called dry ice because with the rise of temperature this solid CO_2 directly passes into gas without going through liquid state.

Dry ice is very good refrigerant and easy to handle and so it is used to preserve meat, fish, butter etc. It is also used in creation of exceedingly low temperature required for research work in the laboratory and as local anaesthetic in surgical operation.

- **Use of CO_2 as fire extinguisher.**

CO_2 is extensively used as fire extinguisher. A fire extinguisher consists of a conical cylindrical metallic vessel (*B*) with a nozzle (*N*) at one end. A strong solution of sodium carbonate is kept in the vessel. A glass ampule (*T*) containing sulphuric acid is placed in the Na_2CO_3 solution. There is a knob (*H*) at the other end of the apparatus. When needed the ampule containing H_2SO_4 can be broken by hitting the knob attached to a rod which reaches the ampule. As soon as the acid comes in contact with the Na_2CO_3 solution, CO_2 is generated inside the metallic vessel which comes out forcibly through the nozzle and is directed towards the fire.

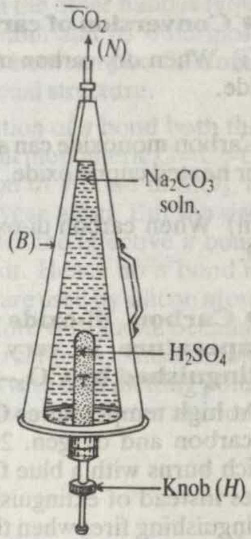


Fig 4.11 : Fire extinguisher

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2\uparrow + H_2O$$

Foam type fire extinguisher :

At present foam type fire extinguishers are used to extinguish oils and petrol fires. Such type of fire extinguishers consist of solutions of *aluminium sulphate* and *sodium bicarbonate* in separate ampules. When required the two ampules are broken and the two solutions are mixed together. $Al_2(SO_4)_3$ undergoes hydrolysis to produce $Al(OH)_3$ and H_2SO_4. The H_2SO_4 thus produced reacts with $NaHCO_3$ to liberate CO_2. The bubbles of CO_2 produce stable foams with $Al(OH)_3$ and these foams are ejected forcibly through the nozzle and applied on the fire where a layer of CO_2 is formed which covers oil. Thus the oil or petrol can not come in contact with air or oxygen. As a result the fire extinguishes.

$$Al_2(SO_4)_3 + 6\,NaHCO_3 = 2Al(OH)_3 + 3Na_2SO_4 + 6CO_2$$

- **Prove that carbon di-oxide contains carbon.**

Pure and dry carbon di-oxide is taken in a gas jar. A piece of burning magnesium ribbon is introduced into the gas jar, when the Mg ribbon continues to burn inside the jar. After the completion of the reaction, a residue is obtained. This residue is treated with dil. HCl when black particles are found to float on the solution. The black particles are filtered, washed and dried and then burnt in oxygen when a colourless and odourless gas is obtained which turns lime water milky. This proves that CO_2 is formed on burning the black particles in oxygen. Thus it is proved that the black particles are nothing but carbon. This carbon comes from carbon di-oxide.

$$2Mg + CO_2 = 2MgO + C$$
$$C + O_2 = CO_2$$
$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$

- **Prove that CO_2 is soluble in water and its aqueous solution is acidic.**

A gas jar full of CO_2 is taken and some water is added to it. After covering the mouth of the gas jar with a lid, it is shaken well and kept inverted on water in a vessel. On removing the lid from the mouth of the gas jar, water gradually rises up inside the jar and fills it almost completely. Now blue litmus solution is added to the solution when it turns dull red.

This is due to the fact that on shaking, the CO_2 inside the jar dissolves in water creating a partial vacuum inside the jar. On inverting the jar on water, water rises up to fill up the empty space. CO_2 dissolves in water producing carbonic acid which turns blue litmus dull red. Thus it is proved that CO_2 is soluble in water and its aqueous solution is acidic.

- **Conversion of carbon monoxide to carbon di oxide and vice versa.**

(i) When dry carbon monoxide is burnt in oxygen, it is converted to carbon dioxide.

$$2CO + O_2 = 2CO_2$$

Carbon monoxide can also be converted to CO_2 when carbon monoxide is passed over heated cupric oxide.

$$CO + CuO = Cu + CO_2.$$

(ii) When carbon di-oxide is passed over red hot coke, CO_2 is reduced to give CO.

$$CO_2 + C = 2CO.$$

- **Carbon di-oxide is harmful in extinguishing fires where the temperature is very high or burning of magnesium can not be extinguished by CO_2—Explain why.**

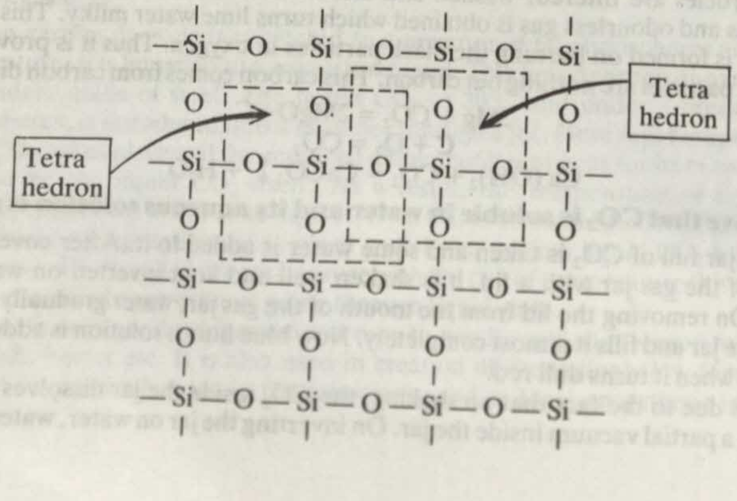
At high temperatures CO_2 is decomposed to give carbon monoxide and oxygen or carbon and oxygen. $2CO_2 = 2CO + O_2$. The CO thus produced is combustible which burns with a blue flame. While O_2 is a supporter of combustion. So in such cases instead of extinguishing the fire, CO_2 aggravates it. Thus CO_2 is harmful in extinguishing fires when the temperature is very high.

Burning magnesium produces a tremendous heat and it continues to burn in CO_2. This is due to the fact that at this high temperature CO_2 is decomposed to give carbon and O_2. The free O_2 thus produced oxidises Mg to form MgO. So the combustion of Mg continues in presence of CO_2.

$$CO_2 = C + O_2$$
$$2Mg + O_2 = 2MgO.$$

- **Explain why, carbon di-oxide is a gas at room temperature but silica is a hard solid with high melting point.**

Crystal structure by X-ray analysis has shown that in silica, each Si atom is sorrounded tetrahedrally by 4 oxygen atoms giving rise to SiO_4 tetrahedron, each oxygen atom being shared with another tetrahedron leading to a three dimensional giant molecular structure.

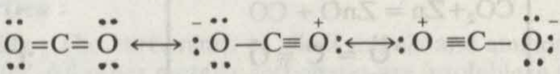


Carbon di-oxide on the other hand is a discrete CO_2 molecule. The inter molecular forces in CO_2 are weak. Again the size of C-atom being very small, the nucleus of C-atom attracts its outermost electrons very firmly and does not allow O-atom to combine with other carbon atoms. The radius of Si-atom on the other hand is large and hence the attraction between the nucleus of silicon atom and its outermost electrons is weak. Hence one oxygen atom may be shared between two Si-atoms giving rise to —Si—O—Si— unit leading to three dimensional structure.

Again C—O can easily form a π bond since in the formation of π bond both the two atoms uses $2p$ orbitals of same size and energy. As a result monomeric O=C=O molecule is formed. On the otherhand in case of formation of π bond in SiO_2, it requires the use of $3p$ orbital of silicon and $2p$ orbital of oxygen atom. But the size and energy of these two p orbitals are quite different. Hence the effective π bond formation between silicon and oxygen atom is very difficult. Hence no π bond is observed in silica molecule. Instead, four sp^3 hybrid orbitals are used by silicon atom to form SiO_4 tetrahedron. Crystal structure of SiO_2 is therefore very stable because of infinite three dimensional structures. To break this structure a considerable amount of energy is required. This explains why silica is hard with high melting point and the discrete molecular structure of CO_2 explain its gaseous character at room temperature.

• The structure of carbon di-oxide :

The structure of carbon di-oxide molecule is linear with the carbon atom at the centre. Carbon di-oxide molecule is non polar and possesses zero dipole moment, although it contains two $\overset{\delta+}{C}—\overset{\delta-}{O}$ bonds each of which is polar. This is due to the fact that the $\overset{\delta+}{C}—\overset{\delta-}{O}$ dipole moment of one side is cancelled by the $\overset{\delta+}{C}—\overset{\delta-}{O}$ dipole moment of the other side, since dipole moment is a vector property. The two oxygen atoms are joined to the carbon atom by double bond. C—O bond distance 1·15Å suggests that CO_2 is a resonance hybrid.



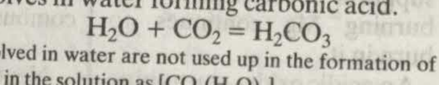
$$\underset{\cdot\cdot}{\ddot{O}}=C=\underset{\cdot\cdot}{\ddot{O}} \longleftrightarrow :\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}—C\equiv\overset{+}{O}: \longleftrightarrow :\overset{+}{O}\equiv C—\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:$$

• Comparison of the properties of Carbon monoxide and Carbon di-oxide.

Properties	Carbon di-oxide (CO_2)	Carbon monoxide (CO)
1. Colour and odour	Colourless and odourless gas.	Colourless gas having a faint smell.
2. Vapour density	Vapour density = 22. 1½ times heavier than air	Vapour density = 14. slightly lighter than air
3. Combustibility	Neither combustible nor supports combustion, but burning Mg continues to burn in it.	Burns with a pale blue flame—does not support combustion.
4. Nature of oxide.	An acidic oxide—turns blue litmus solution wine red, produces carbonic acid with water.	Neutral oxide, does not change the colour of litmus.

Properties	Carbon di-oxide (CO_2)	Carbon monoxide (CO)
5. Action on alkalis	At first forms carbonates and finally forms bi-carbonates when excess of CO_2 is passed. $2NaOH + CO_2 = Na_2CO_3 + H_2O$ $Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$	Does not react with alkali at ordinary conditions but at 200°C and under pressure, it combines with NaOH forming HCOONa. $CO_2 + NaOH = HCOONa$
6. Addition reaction	As it is a saturated compound, it does not form any additive compound.	As CO is an unsaturated compound, it can form additive compounds. $CO + Cl_2 = COCl_2$
7. Absorbant	Completely absorbed by NaOH or KOH solution. $2NaOH + CO_2 = Na_2CO_3 + H_2O$	Absorbed by anmoniacal cuprous chloride solution forming $[CuCl.CO.2H_2O]$
8. Physiological action	Not poisonous—causes death by suffocation due to lack of O_2.	Highly poisonous—combines with the haemoglobin of blood and destroys its ability to carry O_2.
9. Action on lime water	Turns lime water milky. On passing excess of CO_2 the milkiness disappears due to the formation of soluble. $Ca(HCO_3)_2$. $Ca(OH)_2 + CO_2 = CaCO_3 \downarrow + H_2O$ $CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$	Has no action on lime water.
10. Oxidation or reducing property	Has no reducing property itself is reduced to CO, by C. Fe, Zn etc., at high temperatures. $CO_2 + C = 2CO$ $CO_2 + Zn = ZnO + CO$	It is a strong reducing agent, reduces metallic oxides at high temperatures to metals. $CuO + CO = Cu + CO_2$
11. Structure	$\underset{\cdot\cdot}{\ddot{\mathrm{O}}} = \mathrm{C} = \underset{\cdot\cdot}{\ddot{\mathrm{O}}}$	$:\mathrm{C} \overset{\leftarrow}{=} \mathrm{O}:$

Carbon suboxide C_3O_2 : Its structure is linear. $O{=}C{=}C{=}C{=}O$ and is obtained by heating malonic acid with P_2O_5.



$$CH_2\begin{cases}COOH\\COOH\end{cases} \xrightarrow[P_2O_5]{\Delta} C_3O_2 + 2H_2O$$

4.7. Carbonic acid.

Preparation of carbonic acid :

Carbon di-oxide is an acidic oxide. When carbon di-oxide is passed through water, a part of it dissolves in water forming carbonic acid.

$$H_2O + CO_2 = H_2CO_3$$

[Whole of CO_2 thus dissolved in water are not used up in the formation of H_2CO_3. A greater part of the dissolved CO_2 is present in the solution as $[CO_2(H_2O)_n]$.

Properties of H_2CO_3 :

(1) Carbonic acid is very unstable. It has not yet been isolated in the free state. It exists only in aqueous solution. It decomposes on warming with the evolution of CO_2.

$$H_2CO_3 = CO_2 + H_2O.$$

(2) *Carbonic acid is a weak acid.* It is even weaker than many of the organic acids. It ionises as H^+, HCO_3^- and $CO_3^=$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad \text{(bicarbonate ion)}$$
$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^= \quad \text{(carbonate ion)}$$

Due to the presence of H^+ ions in its aqueous solution it exhibits acid property and turns blue litmus wine red.

(3) Carbonic acid is *dibasic* and so it forms two types of salts—(i) *normal salts*—carbonates, (ii) *acid salts*—bicarbonates.

Carbonates are formed by the replacement of both the hydrogen atoms from H_2CO_3

$$2NaOH + H_2CO_3 = Na_2CO_3 + 2H_2O.$$
$$CaCO_3 + H_2CO_3 = CaCO_3 + H_2O.$$

Bicarbonates are formed by the replacement of only one hydrogen atom from H_2CO_3.

$$NaOH + H_2CO_3 = NaHCO_3 + H_2O.$$
$$Ca(OH)_2 + 2H_2CO_3 = Ca(HCO_3)_2 + 2H_2O$$

With the exception of the carbonates of alkali metals and ammonium carbonate, all other normal carbonates are insoluble in water.

Uses : It is used as soft drinks as soda water and lemonade.

4.8. Metallic Carbonates.

General methods of preparation.

(1) *By the action of CO_2 on metallic oxides.*

$$CaO + CO_2 = CaCO_3$$
$$Na_2O + CO_2 = Na_2CO_3$$

(2) *By passing CO_2 through aqueous solution of bases or alkalis.*

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

(3) *By the action of sodium carbonate solution on the salts of alkaline earth or heavy metals.*

$$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl$$
$$CuSO_4 + Na_2CO_3 = CuCO_3 + Na_2SO_4$$

- **Properties :**

(1) **Solubility :** The carbonates of alkali metals and ammonium carbonate are soluble in water. All other metallic carbonates are insoluble in water.

(2) **Action of heat :** The alkali carbonates (Na_2CO_3, K_2CO_3) only melt on strong heating but do not decompose. The carbonates of other metals decompose on strong heating to oxide and CO_2.

$$PbCO_3 = PbO + CO_2$$
$$FeCO_3 = FeO + CO_2$$

(3) **Action on acids :** Any acid when comes in contact with metallic carbonates, CO_2 is evolved with the formation of the salt of the acid.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$
$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2 + H_2O$$

4.9. Metallic bicarbonates.

- **Preparation.**

The bicarbonates of *sodium, potassium, ammonium, calcium, magnesium* can be prepared by passing excess of CO_2 through the solution of the hydroxides.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

- **Properties.**

Bicarbonates are generally soluble in water. On heating, the bicarbonates are decomposed to carbonates with the evolution of CO_2.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$
$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$

Bicarbonates react with acids forming the salt of the acid and CO_2

$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O$$

- Due to the weak nature of carbonic acid, the carbonates of alkali metals (Na_2CO_3, K_2CO_3) react alkaline in aqueous solution due to their hydrolysis.

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^=$$
$$2H_2O \rightleftharpoons 2H^+ + 2OH^-$$

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2(Na^+ + OH^-) + \underset{\text{(weak acid)}}{H_2CO_3}$$

As the aqueous solution of the alkali carbonates produces strong alkali (NaOH or KOH) and weak acid (H_2CO_3) the final solution reacts alkaline due to higher concentration of OH^- ions in the solution. Thus an aqueous solution of a carbonate of alkali metal can be titrated against the solution of strong acids like HCl, H_2SO_4.

The titration takes place in two stages. In the first stage one equivalent of the acid is used to produce the bicarbonate salt and the end point of this reaction is indicated by phenolpthalein indicator.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

Thus phenolpthalein changes the colour when half of the neutralisation takes place. The end point of complete neutralisation is indicated by methyl orange indicator, when the produced $NaHCO_3$ is converted to the normal salt NaCl.

$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O$$

This is why the same volume of Na_2CO_3 solution when titrated with a standard solution of a strong acid using methyl orange indicator, the end point is reached when $2x$ ml of the acid is consumed and using phenolpthalein indicator the end point is reached when only x ml of the acid is consumed.

4.10. Fuels—Coal gas.

Fuels : *A combustible substance which produces heat on ignition in air or oxygen is called fuel.* A fuel always contains *carbon* and *hydrogen*.

The fuel may be solid (wood, coal etc.), liquid (petrol, kerosine etc.) and gaseous (natural gas). In addition to the naturally occurring fuels there are some artificially prepared gaseous fuels, such as *coal gas, producer gas, water gas.*

Producer gas : When a restricted supply of air is passed over white hot coke or charcoal, producer gas is obtained. *Producer gas is chiefly a mixture of carbon monoxide and nitrogen.*

$$2C + \underset{\text{air}}{(N_2 + O_2)} = \underset{\text{producer gas}}{(2CO + N_2)}$$

Water gas : This artificial fuel is obtained by passing steam over white hot coke. *It is a mixture of carbon monoxide and hydrogen.*

$$C + \underset{\text{steam}}{H_2O} = \underset{\text{(water gas)}}{CO + H_2}$$

4.11. Coal gas.

- **What is coal gas—composition of coal gas.**

Coal gas is an artificial gaseous fuel obtained by the destructive distillation of bituminous coal. The composition of coal gas varies with the nature of the coal used and the temperature of distillation. The gaseous constituents of coal gas are divided into three classes.

(1) **Illuminents—light producing gases.**

The unsaturated hydrocarbons which make the flame of the coal gas luminous are—*(i) Ethelene* (C_2H_4), *(ii) Acetylene* (C_2H_2), *(iii) benzene vapour* (C_6H_6)—[2.5−5%].

(2) **Heat producing gases :** The gases which are non-illuminating but produces much heat on combustion are—(i) *Hydrogen* (48-55)%, (ii) *Methane* (CH_4) (26-35)%, (iii) *Carbon monoxide* (4-11)%.

(3) **Inert diluents :** *The gases which are present in coal gas as impurities are—(i) Nitrogen* (2-12)%, (ii) *Carbon di-oxide (0-0.3)%, (iii) Oxygen* (0-1.5)%.

[Carbon monoxide is highly poisonous and due to its presence (4-11)% in *the coal gas, the coal gas is poisonous*].

• Manufacture of Coal gas :

The naturally occurring coal contains various kinds of organic matters, nitrogen, hydrogen, sulphur etc., in combined state in addition to carbon.

Coal gas is manufactured by the destructive distillation of *bituminous coal.*

(i) Powdered bituminous coal is taken in air tight retorts made of fire clay. These retorts are arranged vertically or horizontally in a row and are heated by *producer gas* to about *1000°—1200°C in absence of air.* Thus being carbonised, bituminous coal is decomposed to give a number of variety of products.

(ii) The volatile products given off, pass up a vertical iron pipe called the *ascension pipe* and are led into *hydraulic main* containing water at a fixed level.

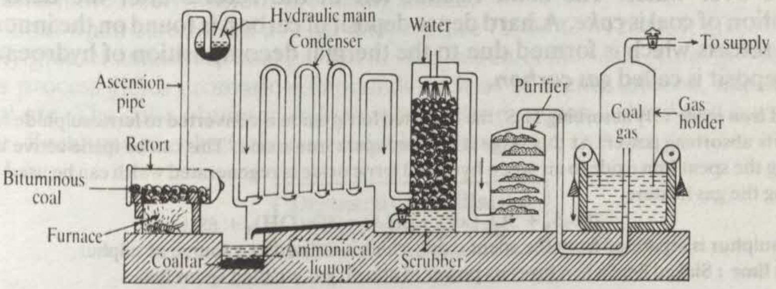


Fig 4.12 : Manufacture of Coal gas

Hydraulic main acts as a water seal which prevents the escaping of coal gas when the retorts are opened for recharging. In hydraulic main the temperature of the volatile products comes down to 60°C and a portion of it condenses into tar and ammoniacal liquor and are collected there.

(iii) The gas mixture coming out of the hydraulic main passes through a series of air or *water cooled condensers.* Here the gas mixture is cooled to atmospheric temperature and hence more tar and ammoniacal liquor separate out and collect in the tar-well in two layers—the upper aqueous colourless layer being *ammoniacal liquor* and the lower black tarry layer being *coal tar.*

(iv) After the separation of coal tar and ammoniacal liquor, the gas mixture contains traces of *CO_2, NH_3, H_2S, HCN, and CS_2 as impurities.* The gas mixture is drawn out of the condensers by means of pump and is led into an iron tower packed with coke, called scrubber, down which a stream of water flows and the gas mixture passes up. The spray of water from the top, washes the gas mixture and practically whole of the ammonia, most of CO_2, tar and some portion of CS_2, HCN and H_2S are removed.

(v) The scrubbed gas mixture still contains some H_2S, CO_2, HCN and CS_2 as impurities. The gas is then led through *purifiers* containing trays of *hydrated ferric oxide* and *slaked lime.*

(a) *Slaked lime absorbs* all CO_2 and some H_2S, HCN and CS_2.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$Ca(OH)_2 + 2H_2S = Ca(HS)_2 + 2H_2O$$
$$Ca(OH)_2 + H_2S + CS_2 = CaCS_3 + 2H_2O$$

(b) *Hydrated ferric oxide* absorbs the last traces of H_2S and HCN.

$$2Fe(OH)_3 + 6HCN = 2Fe(CN)_3 + 6H_2O$$
$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O$$

(c) HCN may also be removed as *ferrocyanide* by passing the gas through a mixture of *caustic soda* and *ferrous sulphate solution.*

$$FeSO_4 + 6HCN + 6NaOH = Na_4[Fe(CN)_6] + Na_2SO_4 + 6H_2O$$

(d) It is not possible to remove CS_2 completely from the gas mixture by the above mentioned process. To remove CS_2 completely, the gas mixture is passed over nickel heated to 450°C, when the hydrogen present in the coal gas reacts with CS_2 producing H_2S which is removed as usual by hydrated ferric oxide.

$$CS_2 + 2H_2 \xrightarrow[\text{Ni cat}]{450°C} 2H_2S + C$$

(vi) The impurities being thus removed, the coal gas is finally stored in big gas holders over water. The solid residue left in the retorts after the destructive distillation of coal is *coke.* A hard dense deposit of carbon is found on the inner walls of the retorts which is formed due to the thermal decomposition of hydrocarbons. This deposit is called *gas carbon.*

Spent iron oxide : By absorbing H_2S, the hydrated ferric oxide is converted to ferric sulphide and then it loses its absorbing power. At this stage it is called spent iron oxide. This can be made active again by exposing the spent iron oxide to air when hydrated ferric oxide is regenerated which can be used again in purifying the gas mixture.

$$2Fe_2S_3 + 3O_2\,(\text{air}) + 6H_2O = 4Fe(OH)_3 + 6S\downarrow$$

Free sulphur is separated from the spent oxide which is utilised as a source of sulphur.

Spent lime : Slaked lime when loses its power to absorb gas is called spent lime.

• By-products of coal gas industry and their uses :

(1) **Coal tar :** It is black, thick and foul smelling viscous liquid. It is a mixture of a large number of valuable organic compounds.

Uses : (i) Coal tar is directly used for preserving timber and water proofing bags. (ii) Fractional distillation of coal tar gives *benzene, toluene, xylene, phenol, aniline, napthalene, creosote oil* etc., which are the starting materials for the production of drugs, dyes, perfumes and explosives. (iii) *Coal tar pitch is* used for road making.

(2) **Ammoniacal liquor :** *It is an aqueous solution of ammonia and ammonium salts like ammonium carbonate, ammonium hydrosulphide* etc. This liquid when boiled with excess of lime produces ammonia.

Uses : It is used to produce *ammonia, ammonium sulphate* and *urea* which are extensively used as important valuable fertilizers.

(3) **Gas Carbon :** It is obtained as a hard dense deposit of carbon on the inner walls of the retorts.

Uses : Gas carbon is used in making *electrodes in electric furnaces, arc lamps* and *electric battaries*. It is also used in *furnace-lining*.

(4) **Coke :** After the completion of the destructive distillation of bituminous coal, coke is obtained as residue in the retort.

Uses : It is used (i) as fuel for cooking purposes, (ii) as *reducing agent* in the extraction of metals. (iii) It is also used in the preparation of *producer gas* and *water gas*.

(5) **Spent iron oxide :** It is obtained in the purifier.

Uses : It is used as a source of sulphur for the production of SO_2 in the manufacture of H_2SO_4 by contact process. It is also used for the production of potassium ferrocyanide.

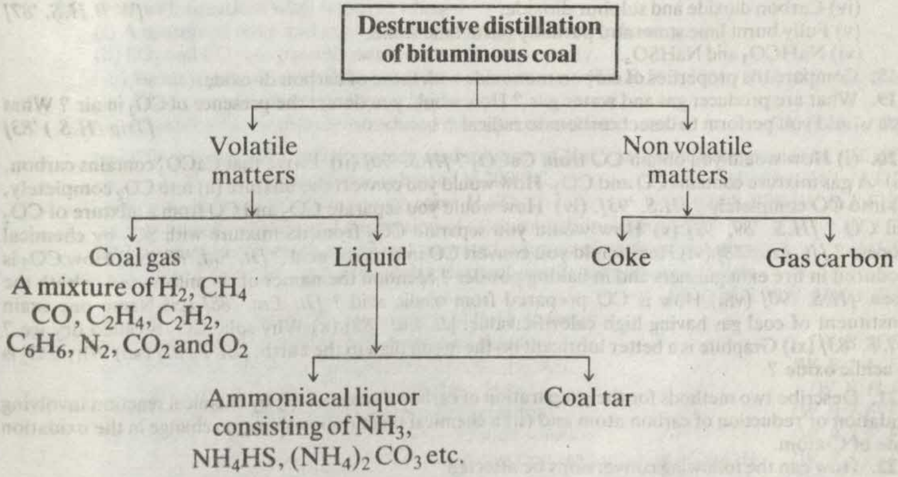
(6) **Spent lime :** It is obtained in the purifier. It is used as fertilizer.

• Carbonisation of Coal :

The destructive distillation of coal is known as *carbonisation of coal*. The quality and quantity of products depends on the temperature of distillation.

(i) Coal carbonised at low temperature (600°C—650°C) gives less amount of coal gas but the produced gas has much higher calorific value and thus it is regarded as *better fuel*. By low temperature process much coal tar is obtained which on fractional distillation yields motor spirit and fuel oils. The coke obtained in this process is soft and burns more freely without producing smoke.

(ii) Coal when carbonised at high temperature (1000°C—1200°C), gives comparatively greater amount of coal gas but having less calorific value. Coal tar obtained in this process yields aromatic compounds such as benzene, toluene, napthalene, phenol etc. The coke obtained in high temperature process is hard and burns with smoke. Such type of coke is used as reducing agent in the metallurgy.


Destructive distillation of bituminous coal
Volatile matters
Non volatile matters
Coal gas
A mixture of H_2, CH_4 CO, C_2H_4, C_2H_2, C_6H_6, N_2, CO_2 and O_2
Liquid
Coke
Gas carbon
Ammoniacal liquor consisting of NH_3, NH_4HS, $(NH_4)_2CO_3$ etc.
Coal tar

• Exercises •

1. What is allotropy ? Name the different allotropes of carbon. Mention their chief uses.

2. How would you prove that diamond and charcoal are the different allotropes of the same element ? *[W.B.H.S. '62]*

3. (a) Describe the preparation of artificial diamond and graphite. Mention the differences in their properties.

(b) A small amount of diamond was alloyed with iron. What products were formed ? How was the chemical nature of diamond disclosed by this experiment ? *[Jt. Ent. '91]*

4. What are the various types of charcoal ? How are they prepared ? What is active charcoal ? Mention some of its uses. Mention some reactions in which active charcoal acts as catalyst.

5. Name the different types of charcoal ? How would you prepare pure charcoal ? Discuss the properties and uses of charcoal. *[Trip (H.S.) '78]*

6. Conc. H_2SO_4 is added to sugar and is heated when a black coloured element is obtained which is insoluble in acids. When it is burnt in O_2, a colourless gas is obtained which turns lime water milky. Identify the element.

7. Mention the differences in the arrangement of carbon atoms in diamond and graphite. What differences in the properties of diamond and graphite are found due to the different arrangement of atoms in them ? What is meant by 0·5 carat diamond ?

8. Compare the properties of the different allotropes of carbon.

9. How is carbon di-oxide prepared in the laboratory ? How is the gas collected ? Name an absorbant of CO_2 and mention one test to identify it.

10. (a) What is dry ice ? How is it prepared ? Mention its important uses.

(b) CO_2 is a product of combustion of carbon, then how magnesium burns in CO_2 ?

11. How is carbon di-oxide converted to carbon monoxide and vice versa ?

Describe experiments to prove that (i) Carbon di-oxide contains carbon *[W.B.H.S. '91]*, (ii) CO_2 can oxidise at high temperature, (iii) The aqueous solution of CO_2 is acidic, (iv) CO contains carbon.

12. Compare the properties of CO_2 with those of SO_2 *[W.B.H.S. '84]*

13. Describe with a neat diagram the laboratory method of preparation of carbon monoxide. How is the gas collected ? Give two examples to illustrate its reducing property. How would you prove that carbon monoxide contains carbon ?

14. How pure carbon monoxide is prepared in the laboratory ? *[W.B H.S. '91]*

15. How would you remove traces of CO from CO_2 and CO_2 from CO ? *[W.B.H.S. '81, '83, '93]*

16. Write short notes on—(i) Active charcoal,(ii) Aerated water, (iii) Dry ice, (iv) Carbonic acid, (v) Carbonates and bicarbonates.

17. Mention one chemical reaction for each case by which you can distinguish between—

(i) Sodium carbonate and sodium bicarbonate. *[W.B.J.E.E. '90]*
(ii) Carbon di-oxide and carbon monoxide. *[W.B.J.E.E. '80, '93]*
(iii) Carbon monoxide and nitric oxide.
(iv) Carbon dioxide and sulphur dioxide. *[W.B.H.S. '87]*
(v) Fully burnt lime stone and partially burnt lime stone.
(vi) $NaHCO_3$ and $NaHSO_4$.

18. Compare the properties of carbon monoxide with those of carbon di-oxide.

19. What are producer gas and water gas ? How would you detect the presence of CO_2 in air ? What tests would you perform to detect carbonate radical ? *[Trip (H.S.) '83]*

20. (i) How would you obtain CO from $CaCO_3$? *[H.S. '90]* (ii) Prove that $CaCO_3$ contains carbon, (iii) A gas mixture contains CO and CO_2. How would you convert the mixture (a) into CO_2 completely, (b) into CO completely ? *[H.S. '93]*. (iv) How would you separate CO_2 and CO from a mixture of CO_2 and CO ? *[H.S. '89, '92]* (v) How would you separate CO_2 from its mixture with SO_2 by chemical process ? *[Jt. Ent. '88]* (vi) How would you convert CO into oxalic acid ? *[Jt. Ent. '88]* (vii) How CO_2 is produced in fire extinguishers and in baking powder ? Mention the names of chemicals used in both the cases. *[H.S. '90]* (viii) How is CO prepared from oxalic acid ? *[Jt. Ent. '88]* (ix) Name one main constituent of coal gas having high calorific value. [*Jt. Ent. '87*] (x) Why solid CO_2 is called dry ice ? *[I.I.T. '83]* (xi) Graphite is a better lubricant on the moon than in the earth. *[I.I.T. '87]* (xii) Why CO_2 is an acidic oxide ?

21. Describe two methods for the preparation of carbon di-oxide—(i) by chemical reaction involving oxidation or reduction of carbon atom and (ii) a chemical reaction involving no change in the oxidation state of C-atom.

22. How can the following conversions be affected

(a) Sugar to carbon di-oxide and carbon monoxide. (b) Carbon monoxide to methanol and formic acid. (c) Carbon di-oxide to carbon monoxide and vice verse. (d) Coke to graphite. (e) Carbon to formic acid. (f) CO_2 to oxalic acid *[Joit Ent '88]*, (g) $CaCO_3 \rightarrow CO$ [*W.B.J.E. '93*], (h) Water gas $\rightarrow CO_2$ [*W.B.J.E. '93*].

23. Explain Why—

(i) Carbon can act both as an abrasive and as a lubricant. *[I.I.T. '89]*
(ii) Presence of carbon monoxide in air is much harmful than CO_2. *[H.S. '92]*
(iii) CO is a fuel.
(iv) Diamond is very hard but graphite is soft. *[W.B.H.S. '85] [Jt. Ent. '79]*
(v) Dilute H_2SO_4 is not used in the preparation of CO_2 from marble. *[W.B.H.S. '83, '93]*
(vi) White crust is formed on the surface of lime water when it is exposed to air. *[W.B.H.S. '79]*
(vii) CO_2 should not be used to fight large fire.
(viii) CO is a reducing agent. *[W.B.H.S. '80]*
(ix) Charcoal and diamond are the two allotropes of the same element. *[W.B.H.S. '81]*
(x) Coal gas is poisonous. *[W.B.H.S. '80, 85]*
(xi) CO_2 is a non polar molecule. *[W.B.J.E.E. '83]*
(xii) CO_2 is non polar while N_2O is polar though both of them have linear structures. *[W.B.J.E.E. '82]*
(xiii) Diamond is a non conductor but graphite is a good conductor of electricity. *[W.B.J.E.E. '87, '89, '92] [W.B.H.S. '91]*
(xiv) Carbon monoxide is combustible but CO_2 is non combustible.
(xv) CO_2 gas can not be dried by lime.
(xvi) CO has both oxidising and reducing properties. *[W.B.H.S. '84]*
(xvii) CO_2 is not poisonous but animals cannot live in it.
(xviii) Bubbles are formed when the cork of a soda water bottle is opened.
(xix) CO_2 cannot extinguish fire caused by Mg. *[W.B.H.S. '87] [I.I.T. '79]*
(xx) CO can form additive compounds but CO_2 cannot.
(xxi) CO_2 cannot reduce while CO can.
(xxii) The melting point of diamond is very high.
(xxiii) When a beaker containing cold water is placed on bunsen burner the outer wall of the beaker becomes hazzy. *[W.B.J.E.E. '88]*
(xxiv) Different allotropes of carbon are the same element. *[W.B.H.S. '87]*
(xxv) Blue flames are produced during the combustion of coal. *[W.B.H.S. '87]*
(xxvi) SiO_2 is a solid while CO_2 is a gas. *[W.B.H.S. '86] [W.B.J.E.E. '83, '89]*
(xxvii) CO_2 acts as fire extinguisher. *[W.B.J.E.E. '90]*
(xxviii) Conc. H_2SO_4 is not used to dry CO gas. *[W.B.J.E.E. '87]*
(xxix) N_2 and CO exhibit similar physical properties.
(xxx) CO_2 is not collected on water at ordinary temperature.

24. What is fuel ? What is coal gas ? Name the main constituents of coal gas. *[W.B.H.S. '87, '88]*

25. Describe briefly the manufacturing process of coal gas. What are the by-products obtained in the preparation of coal gas ? State the uses of each. *[W.B.H.S. '84, '87, '88, '91]*

26. State with equations what happens when—

(i) A mixture of coke and sand is heated strongly in electric furnace.
(ii) SO_2 and CO_2 are passed over red hot coke separately.
(iii) Steam is passed over white hot coke. *[W.B.H.S. '82] [H.S. '90] [Jt. Ent. '87]*
(iv) CO is passed over heated ferric oxide.
(v) A burning magnesium is introduced into a jar of carbon di-oxide. *[W.B.H.S. '82, '89]*
(vi) CO_2 is passed through a concentrated solution of NaCl saturated with ammonia. *[I.I.T. '88]*
(vii) A mixture of coke and lime is heated to 2000°C. *[Jt. Ent. '86] [I.I.T. '78]*
(viii) Sodium formate is heated with conc. H_2SO_4 *[H.S. 87] [W.B.J.E.E. '82]*
(ix) CO_2 is passed through a suspension of calcium carbonate in water. *[I.I.T. '91]*
(x) CO_2 is passed through a cold and saturated solution of sodium carbonate. *[H.S. '74]*
(xi) CO_2 and NH_3 are passed through a slurry of powdered gypsum in water. *[W.B.H.S. '83] [Joint Ent. '84]*
(xii) CO_2 is passed through a suspension of BaO_2 in water.
(xiii) Conc. HNO_3 is heated with powdered charcoal. *[W.B.H.S. '85]*
(xiv) Powdered oxalic acid is heated with conc. H_2SO_4. *[W.B.J.E.E. '83]*
(xv) Powdered charcoal is heated with conc. H_2SO_4. *[W.B.H.S. '74]*
(xvi) A mixture of CO and Cl_2 is exposed to sun light. *[W.B.J.E.E. '85]*
(xvii) Na_2CO_3 solution is added to ferric chloride solution. *[W.B.J.E.E. '83]*
(xviii) CO under pressure is passed through concentrated solution of NaOH. *[W.B.J.E.E. '83]*
(xix) A piece of burning sodium or potassium is introduced into a jar containing CO_2.
(xx) CO_2 is passed through a clear solution of lime water gradually in excess.

(xxi) Excess of CO_2 is passed through a solution of caustic soda and the product is heated.
(xxii) CO_2 is passed into water at high pressure. *[H.S. '92]*
(xxiii) CO_2 is passed through a suspension of limestone in water. *[I.I.T. '91]*
(xxiv) Alumina is heated strongly with carbon and the residue is treated with water.

27. (i) In which condition carbon monoxide would react with water ? Name the products and give equation of the reaction. *[W.B.H.S. '83, '90]*
(ii) How would you detect the presence of small amount of CO in air ? *[W.B.H.S. '83]*
(iii) How would you remove CO from a mixture of CO and CO_2 ? *[W.B.H.S. '83, '93]*
(iv) How will you prove the reducing property of CO ? *[W.B.H.S. '84]*
(v) How would you remove CO_2 from CO. *[Joint Ent. '85]*
(vi) How would you identify CO_2 in which SO_2 is also present ?
(vii) H_2 is present in a sample of CO. How would you identify CO ?
(viii) How you convert NH_3 to $(NH_4)_2SO_4$ without using H_2SO_4 ? *[W.B.J.E.E. '92]*

28. (i) A white solid (A) on being heated gives a white solid (B) and a colourless and odourless gas (C)
(ii) When (B) is treated with dil. HCl gives (C)
(iii) When (C) is passed through NaOH solution at first (B) is formed and then on passing excess of (C), (B) is converted to (A).
(iv) When $CaCl_2$ solution is added to an aqueous solution of (B) a white precipitate (D) is obtained.
(v) (D) dissolves in dil. HCl to produce (C).
Express the above reaction by chemical equation. Mention the two uses of (C).
[*Ans.* A = $NaHCO_3$, B = Na_2CO_3, C = CO_2, D = $CaCO_3$] *[H.S, '87]*

29. A mixture of three gases (A), (B) and (C) is passed through an acidified solution of $K_2Cr_2O_7$ when (A) is absorbed turning the solution green. The remaining gas mixture is passed through lime water when (B) is absorbed turning the lime water milky. The residual gas (C) is absorbed by alkaline pyrogallate solution. The original gas mixture does not turn lead nitrate paper black. Identify (A), (B) and (C).
[*Ans.* A = SO_2, B = CO_2, C = O_2] *[I.I.T. '81]*

30. A colourless gas (B) is produced by the action of dilute H_2SO_4 on a sodium salt (A). When a burning magnesium ribbon is introduced into a gas jar containing (B), yields a white residue (C). When (C) is treated with dil. HCl, a portion of it dissolves leaving a black residue (D). (D) produces (B), when it is burnt in oxygen. Identify (A), (B), (C) and (D). [*Ans.* A = Na_2CO_3, B = CO_2, C = MgO, D = C]

- **Objective type questions :**

1. Which one is the wrong statement ?
Carbon differs from the other elements due to—
(a) its limitation to a co-ordination number four,
(b) there are *d*-orbitals in its penultimate shell.
(c) its unique ability to form multiple bonds.
(d) its marked tendency to form long chain (catenation)

2. Which of the following is a good conductor of heat and electricity ?—
(a) Anthracite, (b) diamond, (c) charcoal, (d) graphite.

3. Wood charcoal is used for decolourisation of sugar because—
(a) it oxidises the coloured material, (b) it reduces the coloured material, (c) it converts coloured material to colourless, (d) it adsorbs coloured material.

4. Dry powder extinguisher contains—
(a) sand, (b) sand and Na_2CO_3, (c) sand and baking powder, (d) sand and K_2CO_3.

5. Graphite is used in the nuclear reactors—
(a) as a lubricant, (b) as a fuel, (c) for lining inside of the reactor as an insulator, (d) for reducing the velocity of neutrons.

6. Diamond and graphite are—
(a) isomers, (b) isotopes, (c) allotropes, (d) polymers.

7. Dry ice is—(a) solid ice without any water, (b) solid SO_2, (c) solid CO_2, (d) solid benzene.

8. Water gas is a mixture of—
(a) H_2O + air, (b) CO + H_2, (c) CO + CO_2, (d) CO + N_2.

9. 'Lead pencil' contains—
(a) Pb, (b) FeS, (c) graphite, (d) PbS. *[I.I.T. '80]*

10. Which of the following is a true acid anhydride ?
(a) Al_2O_3, (b) CO, (c) CaO, (d) CO_2.

11. Which of the following is a crystalline form of carbon ?—
(a) gas carbon, (b) blood charcoal, (c) sugar charcoal, (d) graphite.

12. CO is—(a) an oxidising agent, (b) reducing agent, (c) acidic oxide, (d) none of the above.

13. X rays can pass through—(a) diamond, (b) graphite, (c) glass, (d) gas carbon.

14. In the preparation of CO_2 by the action of marble on acids, dil. H_2SO_4 is not used as H_2SO_4—
(a) is an oxidising agent, (b) a dehydrating agent, (c) forms a layer of insoluble $CaSO_4$ on marble, (d) does not react with marble.

15. The reaction $2Mg + CO_2 = 2MgO + C$ shows that CO_2 is—
(a) a reducing agent, (b) an oxidising, (c) a dehydrating agent, (d) none of the above.

16. The allotropic form of carbon which is used as an abrasive is—
(a) diamond, (b) graphite, (c) charcoal, (d) gas carbon.

17. CO_2 does not match with—
(a) acid anhydride, (b) acidic oxide, (c) producer of carbonates, (d) reducing agent.

18. Sugar contains carbon can be proved by its—
(a) dehydration, (b) oxidation, (c) reduction, (d) hydrolysis.

19. CO_2 forms—
(a) sulphates, (b) carbonates, (c) carbides.

20. CO can form—
(a) acid, (b) alkali, (c) additive compound, (d) none of the above.

21. The chemical name of phosgene is—
(a) phosphine, (b) carbonyl chloride, (c) phosphorus oxychloride, (d) phosphorus tri chloride.

22. Absorbent of carbon monoxide is—
(a) alkaline pyrogallate solution, (b) caustic potash solution, (c) $FeSO_4$ soln., (d) ammoniacal cuprous chloride solution.

5

Phosphorus and Its Compounds

Symbol : P.	Atomic No. : 15	Atomic wt. : 30.98
Electronic configuration :	$1s^2\,2s^2\,2p^6\,3s^2\,3p^3$	Oxidation number : −3, +1, +3, +5

Phosphorus was first discovered by *Brand*— a German alchemist in 1674. He obtained it by the distillation of evaporated urine. In 1772 *Scheele* prepared it by distilling phosphoric acid with charcoal. In 1777 Laviosier established phosphorus as an element.

5.1. Occurrence of phosphorus.

Phosphorus is very active element and so it is not found in free state in nature. In combined state, it is widely distributed in nature as phosphates. The chief minerals of phosphorus are (i) *Phosphorite,* [$Ca_3(PO_4)_2$], (ii) *Chlorapatite,* [$3Ca_3(PO_4)_2$ $CaCl_2$], (iii) *Flourapatite* [$3Ca_3\,(PO_4)_3$, CaF_2], (iv) *Vivianite* [$Fe_3\,(PO_4)_2$, $8H_2O$].

- **Bone ash and bone charcoal :**

Bones contain about 58% *calcium phosphate* small amount of *calcium carbonate, gelatine, fat* and *nitrogeneous organic matters.* (i) At first bones are cut into small pieces and boiled with water. (ii) The bone pieces are then digested with *carbon disulphide* or *carbon tetra chloride* to remove fats and greasy matters from the surface of bones. (iii) Bones being thus freed from fats and grease, are heated in super heated steam by which gelatine is removed from bones. (iv) The bone-pieces are then crushed into powder and subjected to destructive distillation in iron retorts, The volatile matters of bones are distilled off and the black residue that remains in the retort is called *bone charcoal* or *bone black.* Bone charcoal is a mixture of *carbon* and *calcium phosphate.* (iv) Bone charcoal on being calcined in air yields bone ash which contains about 80% of calcium phosphate. Bone ash is the chief source for the preparation of phosphorus.

5.2. Preparation of white phosphorus.

(1) Preparation of white phosphorus from bone ash—old retort process :

(i) Powdered bone ash is mixed with 60% H_2SO_4 and the mixture is heated, when insoluble *calcium sulphate* and *phosphoric acid* are produced.

$$Ca_3\,(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 \downarrow \;\; + 2H_3PO_4$$

Calcium sulphate is removed by filtration and phosphoric acid is obtained as filtrate.

(ii) The phosphoric acid thus obtained is made concentrated by heating to a syrupy liquid.

(iii) Powdered coke is then mixed with this syrup and the mixture is carefully heated to dryness in cast iron vessels, when phosphoric acid is converted to *meta phosphoric acid* (HPO_3).

$$H_3PO_4 = HPO_3 + H_2O.$$

(iv) This dried residue is then taken in fire clay retort, the open end of which is dipped under water. The retort with the contents is strongly heated when meta phosphoric acid is reduced by the coke to produce white phosphorus.

$$4HPO_3 + 12C = P_4 + 12CO + 2H_2$$

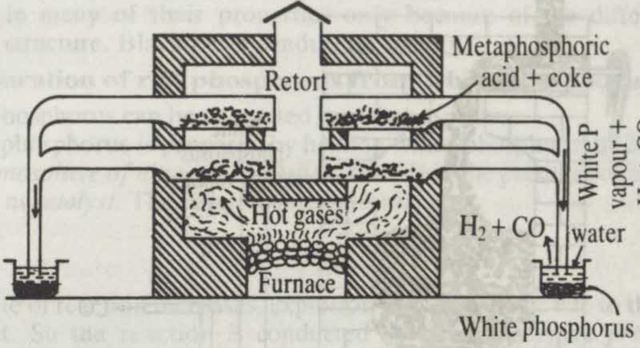


Fig 5.1 : Preparation of white phosphorus from bone ash

(v) The produced carbon monoxide, hydrogen and vapours of white phosphorus escape through the mouth of the retort. The phosphorus vapours condense under water, as a dark brown mass.

(2) Modern electro-thermal process :

This process is also known as *Parker-Robinson-Readmann process* after the names of the discoverers of this process.

[A] **Raw materials :** In this process *phosphate rock* or *bone ash* [$Ca_3(PO_4)_2$], *sand* (SiO_2) and *coke* are used as raw materials.

[B] **Reactions :** A mixture of powdered phosphorite or bone ash, sand and coke is heated to 1500°C in an electric furnace.

The reactions take place in two steps :–

(a) At 1200°C, *calcium phosphate* reacts with *silica* to form *calcium silicate* and *phosphorus pentoxide*.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5 \uparrow$$

(b) At 1500°C phosphorus pentoxide thus obtained is reduced by coke to *white phosphorus* and coke is oxidised to *carbon monoxide*.

$$2P_2O_5 + 10C = P_4 \uparrow + 10CO \uparrow$$

[C] **Electric furnace :** The furnace in which the manufacture of white phosphorus is carried out is made of fire bricks. It is provided with two carbon electrodes near the bottom of the furnace. There is an outlet near the top for the escape of phosphorus vapours and carbon monoxide. There is a slag hole at the bottom of the furnace.

[D] **Procedure :** The mixture of powdered phosphorite, silica and coke is fed into the electric furnace with the help of a hopper and a screw conveyer. After introducing the charge into the furnace a powerful electric arc is struck between the carbon electrodes to produce high temperature. The temperature rises up to 1500°C. At this high temperature reactions take place and phosphorus vapours with carbon monoxide come out of the furnace through the outlet tube and are led into cold water. Phosphorus vapours condense and collect under water as solid. Molten calcium silicate is tapped from the slag hole at the bottom of the furnace.

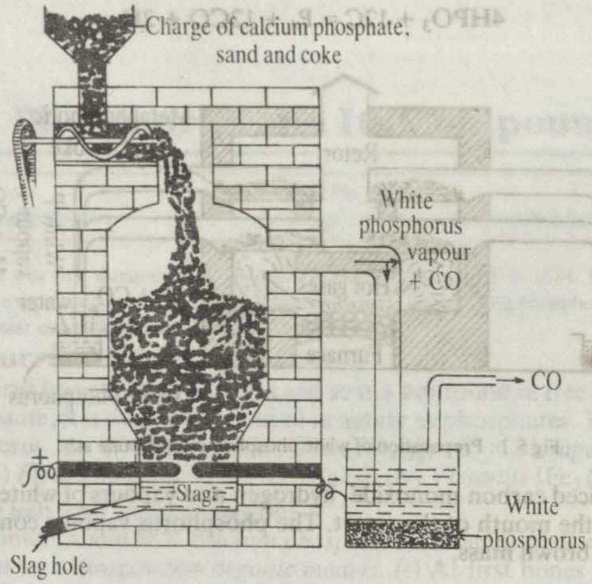

Charge of calcium phosphate, sand and coke
White phosphorus vapour + CO
CO
+
−
Slag
White phosphorus
Slag hole

Fig 5.2 : Preparation of white phosphorus by electrothermal process

[E] **Purification :** The white phosphorus thus produced is not pure—it contains *sand, coke particles* and *other impurties.* (i) The crude phosphorus is *melted* under hot water to remove sand and coke particles. (ii) The molten mass is then stirred with *chromic acid* ($K_2Cr_2O_7$ + conc. H_2SO_4). Some of the impurities are oxidised by chromic acid and pass into solution. The insoluble impurities are separated and rise up as scum. (iii) The molten white phosphorus is then filtered through *chamois leather* by squeezing and then distilled in absence of air. The pure phosphorus vapour is collected under water and cast into sticks.

• Phosphorus pentoxide is more acidic than silica, but at high temperature, silica replaces the more acidic P_2O_5 from calcium phosphate—Explain why :

The reaction of silica with calcium phosphate is represented by the equation $Ca_3(PO_4)_2 + 3SiO_2 \rightleftharpoons 3CaSiO_3 + P_2O_5 \uparrow$ The reaction is reversible and by the forward reaction P_2O_5 is produced. P_2O_5 is an acidic oxide and is volatile at high temperature. The boiling point of silica is much high. At high temperature of the furnace the silica displaces the more acidic and volatile P_2O_5 forming calcium silicate. Thus at high temperature the produced P_2O_5 is continuously eliminated from the system and its concentration is decreased. Consequently to make up the loss of the concentration of P_2O_5 the equilibrium of the reversible reaction is shifted in the forward direction. The high lattice energy of the product calcium silicate also favours this conversion. Consequently, SiO_2 though less acidic than P_2O_5 can replace P_2O_5 from $Ca_3(PO_4)_2$ at high temperature.

• White phosphorus is kept under water—Explain why :

As white phosphorus is highly reactive and readily inflames in air at ordinary temperature, it is preserved under water in a closed container, so that it may not come in contact with air.

[***N.B.*** In the modern process of manufacturing white phosphorus, although electric current is passed through the carbon electrodes, it is not an electrolytic process. The function of electric energy in this process is only to produce high temperature in the furnace. For this reason this process is called *electro thermal process*.]

5.3. Allotropy of phosphorus.

Phosphorus exhibits allotropy. The various allotropic forms of phosphorus are—(i) **White** or **Yellow phosphorus,** (ii) **Red phosphorus,** (iii) **Black phosphorus,** (iv) **Violet phosphorus.**

Of these forms, however, only the White and Red phosphorus are best known allotropes of phosphorus and are of practical importance. These two forms differ markedly in many of their properties only because of the difference in their molecular structure. Black P can conduct electricity.

• Preparation of red phosphorus from white phosphorus :

White phosphorus can be converted to red phosphorus.

(i) Red phosphorus is prepared by heating white phosphorus at 240° — 250°C *in an inert atmosphere of nitrogen or carbon dioxide* in the presence of a trace of *iodine which acts as catalyst.* The reaction is *exothermic*.

$$\text{P (white)} \xrightarrow[\text{I}_2\,\text{catalyst}]{250^\circ\text{C}} \text{P (red)}$$

If the rate of reaction increases, explosion may take place due to the evolution of much heat. So the reaction is conducted at *one atmosphere pressure* and the temperature is never allowed to rise above 250°C.

(ii) **Procedure :** An egg-shaped iron vessel is filled with an inert gas like nitrogen or CO_2. The vessel is provided with an up-right tube closed at the top by a safety valve for the release of excess of pressure which may develop inside the vessel. Two thermometers are inserted in the two holes of the iron vessel. White phosphorus with a trace of iodine is kept inside the vessel and the vessel is carefully heated to 250°C. White phosphorus is slowly converted to red phosphorus.

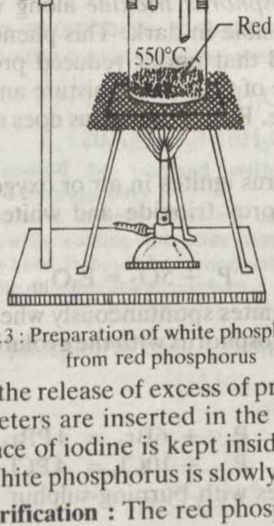


Fig 5.3 : Preparation of white phosphorus from red phosphorus

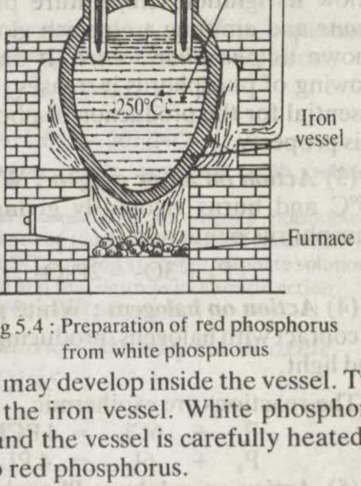


Fig 5.4 : Preparation of red phosphorus from white phosphorus

(iii) **Purification :** The red phosphorus thus obtained is not pure. It may contain some *unchanged white phosphorus.* It is ground to powder under water and then *boiled with strong caustic soda solution,* when any unchanged white phosphorus is removed in the form of phosphine and sodium hypophosphite. $4P+3NaOH+3H_2O$

= $PH_3 + 3NaH_2PO_2$. The red phosphorus is left undissolved in caustic soda. It is washed with water and is dried by air. As red phosphorus does not readily inflame in air, it is not kept under water.

- **Preparation of white phosphorus from red phosphorus.**

Red phosphorus may be readily converted to white phosphorus. Red phosphorus on being heated to 550°C in an inert atmosphere of nitrogen or carbon di-oxide, is vaporised. The vapours of red phosphorus on rapid cooling yields white phosphorus.

$$P\,(\text{red}) \xrightarrow{550^\circ C} P\,(\text{white})$$

5.4. Properties of white and red phosphorus.

- **Properties of white phosphorus :**

[A] **Physical :**

(i) White (yellow) phosphorus is a translucent, waxy, white or light yellow crystalline solid. It is soft enough to be cut easily with knife. (ii) Its boiling point is 288°C and melting poing is 44°C. (iii) Its specific gravity is 1.82. (iv) It is practically insoluble in water but readily dissolves in *carbon di-sulphide*. It is fairly soluble in *carbon tetra chloride, benzene, chloroform* and other organic solvents. (v) It can not conduct heat and electricity. It has an odour reminicent of garlic. (vi) It is very poisonous—about 0.1 g of it if taken internally, is sufficient to cause death. (vii) Continued breathing of small amount of white phosphorus causes decay of bones of the jaws and nose. This is known as *phossy jaw*.

[B] **Chemical :** (1) ***Atomicity*** : Below 1000°C white phosphorus molecule is tetratomic (P_4). At about 1600°C P_4 molecule partially dissociates to form diatomic molecule P_2. $P_4 \rightleftharpoons 2P_2$. At above 1600°C phosphorus becomes monatomic.

(2) ***Phosphorescence*** : In *moist air* white phosphorus undergoes slow oxidation below its ignition temperature producing *phosphorus trioxide* along with some *ozone* and emitting a greenish glow which is visible in dark. This phenomenon is known as *phosphorescence*. It has been found that under reduced pressure the glowing of phosphorus increases. The presence of traces of moisture and ozone is essential for the production of phosphorescence. Red phosphorus does not exhibit this property.

(3) ***Action on air or oxygen*** : White phosphorus ignites in air or oxygen even at 35°C and burns vigorously giving off phosphorus trioxide and white fumes of phosphorus pentoxide.

$$P_4 + 3O_2 = 2P_2O_3\ ; \qquad P_4 + 5O_2 = P_4O_{10}$$

(4) ***Action on halogens*** : White phosphorus ignites spontaneously when it comes in contact with halogens, producing halides of phosphorus with the evolution of heat and light.

The reactions are exothermic.

$$P_4 + 6Cl_2 = 4\,PCl_3\ ; \qquad P_4 + 6Br_2 = 4\,PBr_3$$
$$P_4 + 6I_2 = 4\,PI_3\ ; \qquad P_4 + 10Cl_2 = 4\,PCl_5$$

(5) ***Action on sulphur*** : Phosphorus combines with burning sulphur producing *Phosphours penta sulphide.*

$$P_4 + 10S = 2\,P_2S_5$$

(6) ***Action on strong alkalis*** : White phosphorus reacts with *hot* and *concentrated solution of caustic soda*, or *caustic potash* forming *phosphine* and *hypophosphites.*

However, traces of *hydrogen* and *phosphorus dihydride* are also formed along with phosphine.

$$P_4 + 3NaOH + 3H_2O = PH_3\uparrow + 3NaH_2PO_2$$
$$2P + 2NaOH + 2H_2O = H_2\uparrow + 2NaH_2PO_2$$
$$6P + 4NaOH + 4H_2O = P_2H_4 + 4NaH_2PO_2$$

CaO is treated with water when $Ca(OH)_2$ is formed. Being a strong alkali, when it is heated with white phosphorus in an inert atmosphere, phosphine is liberated and calcium hypophosphite is produced.

$$2P_4 + 3Ca(OH)_2 + 6H_2O = 2PH_3 + 3Ca(H_2PO_2)_2$$

(7) ***Action on metals*** : White phosphorus combines with metals like *copper, sodium, magnesium, aluminium, calcium* etc., producing their corresponding *phosphides*.

$$6Cu + P_4 = 2Cu_3P_2, \qquad 6Mg + P_4 = 2Mg_3P_2$$
$$6Ca + P_4 = 2Ca_3P_2, \qquad 12Na + P_4 = 4Na_3P$$
$$4Al + P_4 = 4AlP$$

Metallic phosphides on treatment with boiling water or dilute acids evolve phosphine.

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3\uparrow$$
$$2AlP + 3H_2SO_4 = Al_2(SO_4)_3 + 2PH_3\uparrow$$

(8) ***Reducing property*** : White phosphorus acts as a reducing agent. In its reducing reactions, it is oxidised to *phosphoric acid*.

(a) *Reduction of nitric acid :* White phosphorus reduces hot and concentrated nitric acid to *nitorgen di-oxide,* itself being oxidised to *ortho phosphoric acid.*

$$\begin{array}{c} [2HNO_3 = H_2O + 2NO_2 + O]\times 5 \\ 2P + 5O = P_2O_5 \\ P_2O_5 + 3H_2O = 2H_3PO_4 \\ \hline 10H\overset{+5}{N}O_3 + 2\overset{0}{P} = 2H_3\overset{+5}{P}O_4 + 10\overset{+4}{N}O_2 + 2H_2O \end{array}$$

It reduces the moderately strong nitric acid to *nitrogen di-oxide* and *nitric oxide.*

$$4\overset{0}{P} + 10H\overset{+5}{N}O_3 + H_2O = 4H_3\overset{+5}{P}O_4 + 5\overset{+2}{N}O + 5\overset{+4}{N}O_2$$

(b) White phosphorus reduces the salts of *copper, silver, gold* in aqueous solutions into the corresponding *metals* which are *precipitated* from the solution.

$$\overset{0}{P}_4+10\overset{+2}{Cu}SO_4+16H_2O=10\overset{0}{Cu}\downarrow+4H_3\overset{+5}{P}O_4+10H_2SO_4$$
$$\overset{0}{P}_4+20\overset{+1}{Ag}NO_3+16H_2O=20\overset{0}{Ag}\downarrow+4H_3\overset{+5}{P}O_4+20HNO_3$$

- **Hands should be washed with $CuSO_4$ solution while working with white phosphorus—Explain why :**

White phosphorus is very corrosive and causes painful burns. It is also highly poisonous. Consequently, while working with white phosphorus, it should not be touched by hands. If accidentally, it is touched by hand, it should be immediately washed with $CuSO_4$ solution as copper sulphate solution reacts with white phosphorus and converts it to phosphoric acid and thus destroys its harmful action.

$$P_4+10CuSO_4+16H_2O=10Cu+4H_3PO_4+10H_2SO_4$$

(c) White phosphorus reduces *concentrated sulphuric acid* to *sulphur di-oxide*.

$$\begin{array}{c} [H_2SO_4=H_2O+SO_2+O]\times 5 \\ 2P+5O=P_2O_5 \\ P_2O_5+3H_2O=2H_3PO_4 \\ \hline 5H_2\overset{+6}{S}O_4+2\overset{0}{P}=2H_3\overset{+5}{P}O_4+5\overset{+4}{S}O_2+2H_2O \end{array}$$

(d) Phosphorus reduces *potassium iodate* to free *iodine* when it is treated with *acidified potassium iodate solution.*

$$2\overset{0}{P}+2K\overset{+5}{I}O_3+H_2SO_4+2H_2O=2H_3\overset{+5}{P}O_4+K_2SO_4+\overset{0}{I}_2$$

• Properties of red phosphorus :

Physical : (i) Red phosphorus is a dark red solid of specific gravity 2·16. (ii) It has no fixed melting point but becomes soft at above 596°C. At higher temperatures it is converted to white phosphorus. (iii) It is insoluble in water and in organic solvents like CS_2, CCl_4, ether, benzene or chloroform. (iv) It is not poisonous. (v) It does not glow in air and it is the stable allotrope of phosphorus at ordinary temperatures.

Chemical : (1) Red phosphorus is much less active than white phosphorus. It is not easily oxidised by air or oxygen and does not exhibit phosphorescence. On being heated in air or oxygen above 260°C, it combines with oxygen forming phosphorus pentoxide.

$$4P+5O_2=2P_2O_5$$

(2) It reacts with the *halogens* slowly forming *halides.* On being heated in *chlorine* it burns in it producing *tri-chloride* and *penta chloride* of phosphorus.

$$P_4+6Cl_2=4PCl_3 \qquad P_4+10Cl_2=4PCl_5$$

It reacts with *bromine* and *iodine* on being heated strongly producing similar compounds.

(3) *Red phosphorus does not react with hot and concentrated solution of strong alkalis like caustic soda* (NaOH) *or caustic potash* (KOH).

(4) On boiling with conc. HNO_3 red phosphorus is oxidised to phosphoric acid and nitric acid is reduced to oxides of nitrogen.

$$\overset{0}{P_4}+10H\overset{+5}{N}O_3+H_2O=4H_3\overset{+5}{P}O_4+5\overset{+2}{N}O+5\overset{+4}{N}O_2$$

• Comparison of the properties of white and red phosphorus. •

Properties	White phosphorus	Red phosphorus
(1) Colour and smell	White, becomes yellow on exposure to air. It has a smell like that of garlic.	Dark red solid having no characteristic smell.
(2) Melting point	Melts at 44°C	It has no definite melting pt. Becomes soft at above 596°C
(3) Ignition temperature.	Ignites at 35°C	Ignites at 260°C
(4) Specific gravity	At 20°C=1·8	At 20°C = 2·2
(5) Solubility	Insoluble in water but soluble in organic solvents e.g., CS_2, CCl_4, $CHCl_3$, benzene etc. This property is used for the separation of white P from Red P.	Insoluble in water as well as in organic solvents.
(6) Chemical activity.	Highly reactive and less stable at ordinary temperature.	Less reactive. It is stable at ordinary temperature.
(7) Phosphorescence	Readily oxidised in air at ordinary temp. producing oxides and emitting greenish glow which is visible in dark.	Not oxidised by air at ordinary temp. Does not exhibit phosphorescence.
(8) Action with chlorine	Readily ignites in Cl_2 forming PCl_3 and PCl_5.	On being heated in Cl_2 it ignites forming PCl_3 and PCl_5
(9) Action on strong alkalis (NaOH, KOH)	Phosphine is evolved with the formation of hypophosphites. $P_4+3NaOH+3H_2O=PH_3+3NaH_2PO_2$	Does not react with NaOH or KOH.
(10) Action on hot and conc. HNO_3	Vigorously reacts with conc. HNO_3 producing phosphoric acid and oxides of nitrogen. $4P+10HNO_3+H_2O=4H_3PO_4+5NO+5NO_2$	Reacts slowly producing phosphoric acid and oxides of nitrogen.
(11) Physiological action	It is very posonous. About 0·1 g of it if taken internally is sufficient to cause death.	It is non poisonous.

5.5. Uses of Phosphorus.

(i) *Match industry :* Formerly white phosphorus was employed for making matches, but because of its poisonous nature it has been replaced by red phosphorus, phosphorus tri sulphide etc.

(ii) *In the manufacture of phosphorus compounds :* Phosphorus is used in the manufacture of phosphoric acid,phosphates, hypophosphites. Hypophosphites are extensively used in medicine as tonics.

(iii) In the manufacture of some alloys. It is used in the manufacture of phosphor bronze (Cu+P+Sn) which is used for making propellers of ship.

(iv) *Phosphides* are used for making 'Holme's signals.

(v) *In radio therapy :* Radio phosphorus (P^{32}) is used in the treatment of blood cancer.

(vi) Red phosphorus is used in the preparation of hydrobromic and hydroiodic acids in the laboratory

(vii) It is used for producing smoke screen during war.

- **Safety matches :**

The tip of the safty match-stick contains a paste of *antimony sulphide, charcoal, potassium dichromate* (or $KClO_3$, Pb_3O_4) and *glue.* To ignite, the tip must be rubbed on a rough surface. The rough surface is prepared by coating a paper with a paste of *red phosphorus, antimony sulphide, powdered glass* and *gum.* The paper after drying is pasted on the two sides of the match box. On rubbing the tip of the stick on the rough surface, heat is generated due to friction which is enough to start the reaction between red phosphorus and the oxidising agents, e.g. $K_2Cr_2O_7$, $KClO_3$, and antimony sulphide (Sb_2S_3). As a result the tip of the stick burns.

5.6. Structure of white and red phosphorus

• White phosphorus is highly reactive and much less stable while red phosphorus is much less reactive but fairly stable—Explain why :

White phosphorus is soft, highly reactive element having low melting point, while red phosphorus is hard and much less reactive form, having high melting point. These remarkable differences between the two forms can be explained in the light of their molecular structures.

The vapour density of white phosphorus determined at 500°C is nearly 62 which corresponds to its P_4 molecular structure. Structural studies of this molecule show that the four P atoms are situated at the four corners of a tetrahedron and are linked to one another by single covalent bond—the P—P bond length being 2·21Å. Each P-atom is bonded to other three P-atoms and each of the P-atom has one unused electron pair. Thus white phosphorus consists of tetrahedrally arranged P_4 units, the P—P—P bond angle being 60°. The magnitude of P—P—P bond angle produced by the overlap of '*p*' orbitals should be 90° and not 60°. As the P—P—P angle in P_4 molecule is less by 30° than the required angle of 90°, the P-atoms in this particular structure are under considerable strain. Hence the P-atoms in its molecule have tendency to be detached from each other and as a result white phosphorus is very unstable and highly reactive. The intermolecular forces acting between the molecules of white phosphorus are very weak and this accounts for its softness, low density and low melting point.

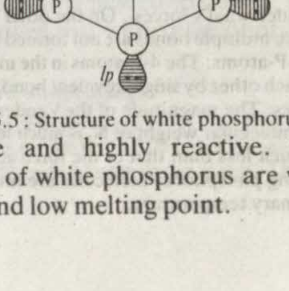
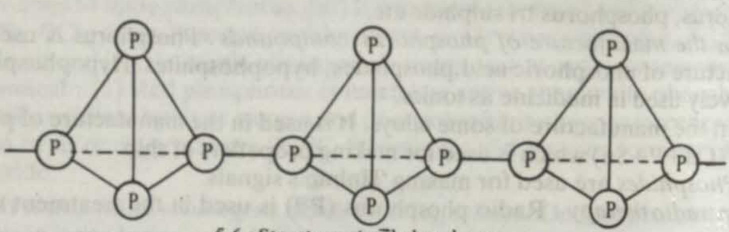


Fig 5.5 : Structure of white phosphorus

On the other hand red phosphorus is *polymeric and made of tiny crystals in* which several P_4 tetrahedron units are linked together by P—P covalent bonds in the form of a long chain. The P-atoms under such structure are relieved of the strain present in tetrahedral P_4 units. Consequently red phosphorus is much stable, more denser and less reactive than white phosphorus. As much heat energy is needed to break this chain structure, the melting point of red phosphorus is much higher than that of the white phosphorus.



5.6 : Structure of red phosphorus

• Prove that white phosphorus and red phosphorus are the different allotropes of the same element :

(i) Equal amounts of pure white phosphorus and red phosphorus are heated separately in excess of pure and dry oxygen. It is found that exactly the same amounts of P_2O_5 are formed in both the cases. Thus it is proved that white and red phosphorus are the different allotropes of the same element.

$$4P(\text{White}) + 5O_2 = 2P_2O_5$$
$$4P(\text{Red}) \;\; + 5O_2 = 2P_2O_5$$

(ii) *m* g of white phosphorus is heated with a trace of iodine at 250°C in an inert atmosphere of nitrogen when *m* g of white phosphorus is completely converted to red phosphorus. The amount of red phosphorus thus obtained is found to be exactly *m* g.

The same amount of red phosphorus on being heated to 550°C in an inert atmosphere of nitrogen, the red phosphorus is converted to vapours, which on rapid cooling condense to form exactly *m* g of white phosphorus.

$$\underset{m\,\text{g}}{P(\text{white})} \xrightarrow[I_2\,\text{catalyst}]{250°\text{C}} \underset{m\,\text{g}}{P(\text{red})}$$
$$\underset{m\,\text{g}}{P(\text{red})} \xrightarrow[\text{Vapours on cooling}]{550°\text{C}} \underset{m\,\text{g}}{P(\text{white})}$$

Thus it is conclusively proved that white phosphorus and red phosphorus are the two allotropes of the same element.

• Nitrogen and phosphorus belong to the same group in the periodic table, but nitrogen is a gas while phosphorus is a solid at ordinary temperature—Explain why.

Nitrogen molecule is diatomic. Due to smaller size of the N-atom, it can undergo sidewise overlap and as a result two π bonds are formed between two N-atoms. Thus the two N-atoms are linked to each other by one sigma and two π bonds ($N\equiv N$). The discrete nitrogen molecules are held together by weak Vander-waal's forces . On the other hand, as P atoms are bigger, sidewise overlap is not possible, and hence multiple bonds are not formed between two P atoms. As a result, the phosphorus molecule consists of 4-P-atoms. The 4-P-atoms in the molecule are arranged at the four corners of a tetrahedron and linked to each other by single covalent bond. The forces acting among the P molecules are called Vander-waal's forces. The magnitude of the Vander-waal's forces is directly proportional to the molecular weight. As the molecular weight of N_2 is much less than that of P_4, the force acting between the nitrogen molecules is much less than that of the force acting between P_4 molecules. Thus the Vander-waal's forces acting among phosphorus molecules are much strong. This is why phosphorus is solid and nitrogen is a gas at ordinary temperature.

• Experiment to illustrate the reducing property of phosphorus.

(i) White phosphorus and conc. HNO_3 are taken in a test tube and gently warmed. After a while brown fumes are found to evolve from the mouth of the test tube. Thus it is proved that white phosphorus reduces nitric acid to produce brown fumes of nitrogen di-oxide.

$$4P + 10\,H\overset{+5}{N}O_3 + H_2O = 4H_3PO_4 + 5\overset{+2}{N}O + 5\overset{+4}{N}O_2$$

(ii) An aqueous solution of $CuSO_4$ is taken in a test tube. A small piece of white phosphorus is dissolved in ethyl alcohol and the solution is added to the $CuSO_4$ solution. The mixture is agitated when a red precipitate is obtained. This precipitate is filtered and washed with water. It is then dissolved in HNO_3 when a blue solution is obtained. Now excess of NH_4OH is added to this solution when a deep blue solution is obtained which is nothing but the solution of cupro ammonium salt. Thus it is proved that the red precipitate is metallic copper. Copper sulphate solution being reduced by white P, has produced the red precipitate of metallic copper.

$$P_4 + 10\overset{+2}{Cu}SO_4 + 16H_2O = 10\overset{0}{Cu}\downarrow + 4H_3PO_4 + 10H_2SO_4$$

• Spontaneous oxidation of phosphorus vapour in air—production of cold flame.

Some pieces of white phosphorus are taken in a round bottomed flask fitted with a long bent tube at right angle and a short tube. The end of the long tube reaches the bottom of the flask. The white phosphorus is covered with glass wools. CO_2 is passsed through the long tube to remove the air inside the flask. The flask is then heated on water bath. Phosphorus vapours come out of the exit tube and as soon as the vapours come in contact with air, a greenish flame is produced at the mouth of the exit tube. The flame does not burn paper or a match stick when placed in it. For this reason, this flame is called *cold flame*. This cold flame is produced by the spontaneous oxidation of white phosphorus vapours by the oxygen of air.

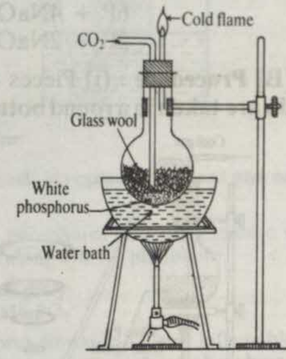


Fig 5.7 : Production of cold flame

• Experiment to illustrate that white phosphorus is more active than red phosphorus.

(i) A piece of white phosphorus is brought in contact with air at ordinary temperature. After a while the piece of white phosphorus inflames producing white fumes of its oxide. White phosphorus combines with oxygen of air at ordinary temperature producing phosphorus trioxide and phosphorus pentoxide.

A piece of red phosphorus on being exposed to air at an ordinary temperature does not inflame. This shows that red phosphorus does not combine with the oxygen of air at an ordinary temperature.

(ii) A piece of white phosphorus is brought in contact with chlorine at ordinary temperature. It ignites spontaneously as soon as it comes in contact with chlorine with the formation of PCl_3 and PCl_5. When red phosphorus is heated to 250°C, it reacts with chlorine to form PCl_3 and PCl_5. Thus it is proved that white phosphorus is more active than red phosphorus.

• White phosphorus has a strong affinity for oxygen—fire under water.

A small piece of white phosphorus is taken in a hard glass test tube containing water. It is heated to 60°C on water bath, when white phosphorus melts. Now oxygen gas is passed through the molten mass of white phosphorus with the help of a tube. Molten phosphorus ignites and burns under water. This proves that white phosphorus has a strong affinity for oxygen.

• HYDRIDES OF PHOSPHORUS •

Phosphine or phosphoretted hydrogen (PH_3)

Phosphine (PH_3) and *phosphorus dihydride* (P_2H_4) are the best known hydrides of phosphorus. PH_3 is a gas while P_2H_4 is a liquid.

5.7. Preparation of phosphine.

• Laboratory method.

[A] **Principle :** Phosphine is prepared in the laboratory by heating *white phosphorus* with *concentrated solution of caustic soda* (or *caustic potash*) in an inert atmosphere of carbon di-oxide or coal gas. Phosphine is liberated as a gas and sodium hypophosphite is produced which remains in the solution. Traces of phosphorus di-hydride (P_2H_4) and H_2 are also produced along with phosphine.

$$P_4 + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$$
$$6P + 4NaOH + 4H_2O = P_2H_4 + 4NaH_2PO_2$$
$$2P + 2NaOH + 2H_2O = H_2 + 2NaH_2PO_2$$

[B] **Procedure :** (i) Pieces of white phosphorus and 30–35% solution of caustic soda are taken in a round bottomed flask fitted with a delivery tube and an inlet tube. (ii) The end of the inlet tube is dipped in the alkali solution inside the flask. (iii) The free end of the delivery tube is dipped under water in a pneumatic trough. (iv) The flask is then clamped to a stand and placed on a wire gauze on a tripod stand. (v) The air inside the flask is completely removed by passing a current of coal gas through the inlet tube. (vi) The flask is now heated by a burner when phosphine is evolved along with a trace of phosphorus dihydride (P_2H_4) and H_2. (vii) The evolved gas passes through the delivery tube and comes out of water of the pneumatic trough producing bubbles. As each bubble escapes out of water and comes in contact with air, it inflames spontaneously with a bright flash forming a vortex ring of white smoke rising up in air.

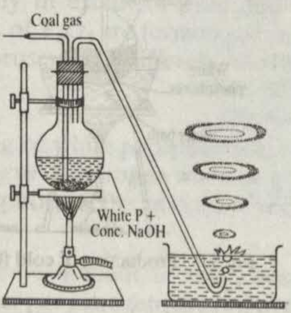


Fig 5.8 : Preparation of phosphine in the laboratory

The white smoke is due to the oxidation of phosphine by the atmospheric oxygen by which fine particles of phosphorus pentoxide are formed.

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$$

[C] **Purification :**

(i) Phosphine thus produced is not pure. Traces of phosphorus dihydride (P_2H_4) and hydrogen are present with the produced phosphine. P_2H_4 is removed by passsing the gas through a U-tube kept in a freezing mixture. P_2H_4 condenses as a liquid and collects in the U-tube, while phosphine passes out and is collected on water. Phosphine may be dried by passing it over solid KOH or phosphorus pentoxide.

(ii) The phosphine produced by laboratory method contains P_2H_4, H_2 and moisture. It is passed through cuprous chloride acidified with HCl. Phosphine is absorbed in this solution with the formation of an addition product Cu_2Cl_2, PH_3. As P_2H_4 and H_2 do not react with acidified Cu_2Cl_2 solution, pass out of the solution. The product Cu_2Cl_2, PH_3 on being heated liberates PH_3 which is dried by KOH or by P_2O_5.

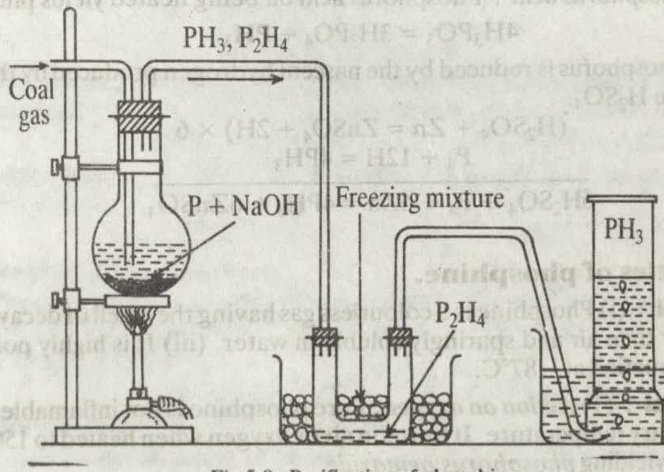


Fig 5.9 : Purification of phosphine

- **The air inside the flask in which phosphine is produced, is replaced by coal gas or by any other inert gas—Explain why.**

During the preparation of phosphine by the action of white phosphorus on boiling caustic soda solution, traces of phosphorus dihydride (P_2H_4) are also produced along with the phosphine.

$$P_4 + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$$
$$6P + 4NaOH + 4H_2O = P_2H_4 + 4NaH_2PO_2$$

Pure phosphine does not inflame in air spontaneously. Phosphorus dihydride is highly inflamable ; it inflames spontaneously as soon as it comes in contact with the oxygen of air. Now phosphine is a combustible gas, so it burns when ignited. If the flask, in which PH_3 is prepared, contains air, the produced P_2H_4 catches fire in contact with the air and the burning of P_2H_4 ignites the phosphine present in the flask. The PH_3 burns to produce P_2O_5. Thus the produced gas inside the flask may cause explosion. To avoid accident, the air inside the reaction flask is replaced by coal gas or any other inert gas.

- **Why does impure phosphine ignite when it comes in contact with air ?**

Phosphine is a combustible gas, but it does not ignite spontaneously in air, P_2H_4 is highly inflamable and inflames spontaneously when it comes in contact with air. During the preparation of phosphine by the action of white phosphorus on NaOH, traces of P_2H_4 are also produced along with the phosphine.

$$4P + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$$
$$6P + 4NaOH + 4H_2O = P_2H_4 + 4NaH_2PO_2$$

Consequently when a mixture of these two gases comes in contact with air. P_2H_4 first catches fire and the burning P_2H_4 gas ignites phosphine which burns producing white smoke of P_2O_5.

5.8. Other methods of preparation of phosphine.

(i) *By the action of water or mineral acids on metallic phosphides*. Metallic phosphides, such as *calcium phosphide, aluminium phosphide* etc., on being treated with boiling water or mineral acids yield phosphine.

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$$
$$2AlP + 3H_2SO_4 = Al_2(SO_4)_3 + 2PH_3$$

(ii) *By the action of strong alkali on phosphonium salts. phosphonium iodide* on being heated with 30% solution of *castic soda* or *caustic potash* yields pure phosphine. The pure PH_3 thus produced is dried by P_2O_5 and is collected on mercury.

$$PH_4I + KOH = KI + PH_3 + H_2O$$

(iii) *From phosphorus acid :* Phosphorus acid on being heated yields phosphine.

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$

(iv) White phosphorus is reduced by the nascent hydrogen produced by the action of zinc on dilute H_2SO_4.

$$\begin{array}{c} (H_2SO_4 + Zn = ZnSO_4 + 2H) \times 6 \\ P_4 + 12H = 4PH_3 \\ \hline 6H_2SO_4 + P_4 + 6Zn = 4PH_3 + 6ZnSO_4 \end{array}$$

5.9. Properties of phosphine.

[A] **Physical :** (i) Phosphine is a colourless gas having the smell of decaying fish. (ii) It is heavier than air and sparingly soluble in water. (iii) It is highly poisonous. (iv) It can be liquefied at −87°C.

[B] **Chemical :** (1) ***Action on oxygen*:** Pure phosphine is not inflamable in air or oxygen at ordinary temperature. It burns in air or oxygen when heated to 150°C with mild explosion yielding *phosphorus pentoxide*.

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$$

(2) ***Basic character*** : Phosphine is *feebly basic* though it is neutral to litmus. It forms unstable *phosphonium halides* with *halogen hydracids*. Its basic nature is exhibited by the formation of these salts.

$$PH_3 + HCl = PH_4Cl \; ; \quad PH_3 + HI = PH_4I$$

A mixture of PH_3 and dry hydrogen chloride does not react at atmospheric pressure but if cooled to −35°C or under 18 atmosphere pressure at 15°C, white cubic crystals of PH_4Cl are deposited.

Phosphonium salts react with strong alkalis like NaOH or KOH to liberate pure phosphine.

$$PH_4I + NaOH = NaI + PH_3 + H_2O$$

(3) ***Action of heat*** : When phosphine is heated to 440°C in a sealed tube in absence of air, it decomposes to give red phosphorus and hydrogen.

$$2PH_3 = 2P(\text{red}) + 3H_2$$

(4) ***Action on chlorine*** : Phosphine ignites spontaneously in *chlorine* yielding *phosphorus tri* and *penta chloride*.

$$PH_3 + 3Cl_2 = PCl_3 + 3HCl \; ; \quad PH_3 + 4Cl_2 = PCl_5 + 3HCl$$

(5) ***Reducing property*** : Phosphine is more powerful reducing agent than ammonia. It forms a black precipitate of *copper phosphide* when it is passed through *copper sulphate solution*.

$$3CuSO_4 + 2PH_3 = Cu_3P_2 \downarrow + 3H_2SO_4$$

(a) Phosphine reduces *silver nitrate solution* to metallic *silver*. At first phosphine reacts with $AgNO_3$ producing *yellow additive compound* which is decomposed by water to give black precipitate of *metallic silver*.

$$PH_3 + 6AgNO_3 = Ag_3P, 3AgNO_3 + 3HNO_3$$
$$Ag_3P, 3AgNO_3 + 3H_2O = 6Ag \downarrow + 3HNO_3 + H_3PO_3$$

(b) Phosphine reduces *nitrous oxide* or *nitric oxide* to *nitrogen.* When a mixture of nitrous oxide and phosphine or nitric oxide and phosphine is sparked, reaction takes place with the formation of N_2 and *phosphoric acid.*

$$PH_3 + 4\overset{+1}{N_2}O = H_3PO_4 + 4\overset{0}{N_2}$$

$$PH_3 + 4\overset{+1}{N}O = H_3PO_4 + 2\overset{0}{N_2}$$

(6) ***Formation of additive compounds*** : Phosphine forms additive compounds when it is passed through a solution of *cuprous chloride* or *aluminium chloride.*

$$Cu_2Cl_2 + PH_3 = Cu_2Cl_2, PH_3; \qquad AlCl_3 + PH_3 = AlCl_3, PH_3$$

(7) ***Absorbant*** : Phosphine is completely absorbed by a *mixture of water* and *bleaching power.*

$$3Ca(OCl)Cl + 3H_2O + PH_3 = PCl_3 + 3HCl + 3Ca(OH)_2$$

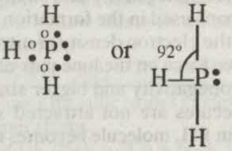
- **Tests of phosphine :**

(i) Phosphine may be identified by its smell of decaying fish. (ii) Phosphine may also be detected by the formation of *black precipitate of cupric phosphide* when it is passed through *$CuSO_4$ solution.*

$$3CuSO_4 + 2PH_3 = Cu_3P_2 \downarrow + 3H_2SO_4$$

- **The structure of PH_3 molecule :**

The electron dot structure of phosphine molecule is shown below. The lone pair of electrons of P-atom in phosphine molecule are present in pure *s* orbital. The H—P—H bond angle in PH_3 molecule is 92°.



5.10. Uses of Phosphine.

(i) Phosphine is used in producing thick smoke which is used as smoke screen in warfare.

(ii) It is used in preparing **Holme's signals.**

A mixture of *calcium carbide* and *calcium phosphide* is packed in a tin vessel having holes at the top. This is thrown into the sea near a rock. Water enters the vessel and reacts with Ca_3P_2 and CaC_2 to produce phosphine and acetylene respectively. Phosphine gets ignited as it comes in contact with air and ignites acetylene. A bright red flame is formed accompanied by huge smoke owing to the burning of PH_3. The light of the burning gases indicates the position of the rock to the approaching ships.

$$Ca_3P_2 + H_2O = Ca(OH)_2 + PH_3$$

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

- **To prove that phosphine contains phosphorus.**

That phosphorus is present in phosphine can be proved by the following process—

A mixture of phosphine and nitrous oxide is subjected to electric spark when phosphoric acid is obtained.

$$PH_3 + 4N_2O = H_3PO_4 + 4N_2 \uparrow$$

The phosphoric acid is evaporated to a syrupy consistency by heat and then mixed with powdered coke. The mixture is heated carefully to dryness when phosphoric acid is converted to *metaphosphoric acid.*

$$H_3PO_4 = HPO_3 + H_2O$$

The dried residue is heated strongly and the vapours produced are passed through cold water when a white solid deposits under water. This solid when brought in contact with air, burns spontaneously at ordinary temperature. It dissolves in CS_2. Thus it is proved that the white solid is white phosphorus and this has come from phosphine.

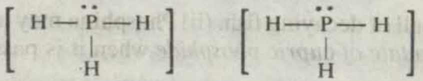
$$4HPO_3 + 12C = 2H_2 + P_4 \uparrow + 12CO \uparrow$$

• The melting point or the boiling point of phosphine is much less than that of ammonia—Explain why.

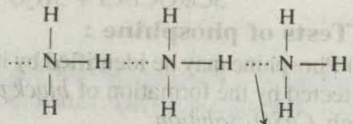
The molecular weight of phosphine is double that of ammonia. Consequently the boiling point of phosphine should have been greater than that of ammonia. But in practice phosphine boils at much lesser temperature than ammonia. This is due to the existence of inter-molecular hydrogen bonding among the molecules of ammonia.

Because of the higher electro-negativity and smaller size of nitrogen atom as compared to those of phosphorus, ammonia molecules are able to get associated by hydrogen bonding. Thus a large number of ammonia molecules get associated by hydrogen bonding and as a result the effective molecular weight of such associated molecules of ammonia becomes much higher than that of the discrete phosphine molecules. Consequently, grater amount of heat energy is required to break these hydrogen bonds among the ammonia molecules.

On the other hand, due to the low electro-negativity and bigger size of phosphorus atom, phosphine can not undergo such association through hydrogen bonding and remains only as mono molecular form. As a result, the boiling and melting points of phosphine is much lower than that of ammonia.



Discrete phosphine molecules

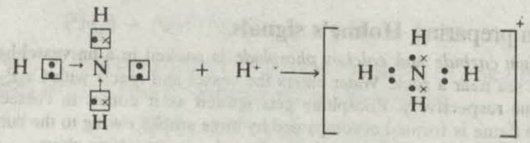


Associated ammonia molecules

• Ammonia is much stronger base than phosphine—Explain why.

The basic character of a compound depends on its tendency to donate its lone pair of electrons to the proton of an acid. Each of the nitrogen atom in ammonia and the phosphorus atom in phosphine contains a lone pair of electrons. Due to the strong electronegativity and small size of N-atom, it has a strong affinity for electrons. Consequently the electrons used in the formation of N—H bonds in ammonia are drawn towards the nitrogen atom. As a result the electron density of nitrogen atom in ammonia becomes greater. This electron density exerts a repulsive force on the lone pair of electrons in nitrogen atom.

On the other hand due to the lower electronegativity and bigger size of P-atoms, the electron pairs forming P—H bonds in the phosphine molecules are not attracted so closely towards the P-atom. Consequently the electron density of P-atom in PH_3 molecule becomes much less than that of ammonia. As a result the N-atom of ammonia can donate its lone pair of electrons more freely to a proton than the P-atom in phosphine. That is why ammonia is stronger base than phosphine.



[N.B. : The lone pair on nitrogen atom in NH_3 molecule is present in sp^3 hybrid orbital having 25% *s*-character, while the lone pair in P-atom in PH_3 is present in pure 3*s* orbital having 100% *s*-character. Larger the *s*-character of an orbital, stronger is the force of attraction between the orbital and the nucleus. Hence the lone pair in PH_3 molecule is firmly bound, making it less available for the protonation and thus PH_3 is less basic. Again as the *p*-character of an orbital increases, its donor ability also increases. Hence the lone pair in NH_3 molecule, having 75% *p*-character, is more available for protonation than the lone pair of PH_3 molecule having no *p*-character. It follows therefore, NH_3 is more basic than PH_3.]

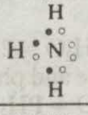
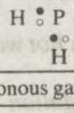
• Phosphine is stronger reducing agent than ammonia—Explain why.

The more an atom has a tendency to lose its electrons, the stronger is its reducing action. Due to the stronger electronegativity and smaller size, N-atom has a greater tendency to attract electrons. On the other hand due to the lower electronegativity and relatively bigger size of P-atom, it has a greater tendency to lose electrons than nitrogen atom. Thus the P-atom in PH_3 can easily increase its oxidation state from (−3) to (+3) or (+5), while N-atom of ammonia cannot increase its oxidation state so easily. Thus by increasing its oxidation state from (−3) to (+3) or (+5), the P-atom in PH_3 is oxidised and this oxidation is brought out by reducing the others. As for example, phosphine reduces $AgNO_3$ to metallic silver at ordinary temperature ; itself being oxidised to H_3PO_3.

$$6AgNO_3 + PH_3 = Ag_3P, 3AgNO_3 + 3HNO_3$$
$$Ag_3P, 3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3PO_3$$
$$6\overset{+1}{Ag}NO_3 + \overset{-3}{P}H_3 + 3H_2O = 6\overset{0}{Ag} + H_3\overset{+3}{P}O_3 + 6HNO_3$$

On the otherhand ammonia cannot reduce silver nitrate. However, at elevated temperatures ammonia can reduce metallic oxides of less electropositive character.

5.11. Comparison between phosphine and ammonia.

Properties	Ammonia (NH_3)	Phosphine (PH_3)
(1) Colour and smell	Colourless gas having a pungent smell.	Colourless gas having a smell of decaying fish.
(2) Density	Lighter than air.	Heavier than air.
(3) Solubility	Highly soluble in water.	Sparingly soluble in water.
(4) Basic property	Basic in character—with water forms weak alkali,—turns red litmus blue and reacts with acids forming ammonium salts. $NH_3 + HCl = NH_4Cl$	Feebly basic in character,—has no action on litmus, reacts with acids, forming phosphonium salts. $PH_3 + HCl = PH_4Cl$
(5) Action on Cl_2	With excess Cl_2 forms NCl_3 which undergoes hydrolysis. $NH_3 + 3Cl_2 = NCl_3 + 3HCl$ $NCl_3 + 3H_2O = NH_3 + 3HOCl$	Ignites spontaneously in Cl_2 forming PCl_3 and PCl_5 which undergoes hydrolysis. $PH_3 + 3Cl_2 = PCl_3 + 3HCl$ $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$
(6) Combustion	Not combustible and does not support combustion, but burns with a yellow flame in an atmosphere of O_2. $4NH_3 + 3O_2 = 2N_2 + 6H_2O$	A combustible gas but does not support combustion, burns in O_2 with the formation of P_2O_5. $2PH_3 + 4O_2 = P_2O_5 + 3H_2O$
(7) Reducing property	Reduces metallic oxides at elevated temperatures. $3CuO + 2NH_3 = 3Cu + N_2 + 3H_2O$	A strong reducing agent ; reduces silver nitrate to metallic silver at ordinary temperature. $6AgNO_3 + PH_3 = Ag_3P, 3AgNO_3 + 3HNO_3$ $Ag_3P, 3AgNO_3 + 3H_2O = 6Ag\downarrow 3HNO_3 + H_3PO_3$
(8) Action on metallic salts	Precipitates metallic hydroxides on being treated with their salts, with some salts produces soluble complex salts on addition of excess of ammonia $FeCl_3 + 3NH_4OH = Fe(OH)_3\downarrow + 3NHCl$	Precipitates metals or metallic phosphides on being treated with the salts of Cu Ag, Au etc. $3CuSO_4 + 2PH_3 = Cu_3P_2\downarrow + 3H_2SO_4$
(9) Molecular structure	3 hydrogen atoms are linked to N-atom by single covalent bonds. With the lone pair of electrons it can form ammonium salts by co-ordinate covalency.  	3 hydrogen atoms are linked to P-atom by single covalent bonds. With the lone pair of electrons, it can form phosphonium salts 
(10) Physiological action	A non poisonous gas.	Highly poisonous gas.
(11) Decomposition	It decomposes at into its elements under electric sparks. $2NH_3 \rightarrow N_2 + 3H_2$	It decomposes at 440°C in a sealed tube into hydrogen and red phosphorus. $2PH_3 \rightarrow 2P + 3H_2$

OXIDES OF PHOSPHORUS

The chief oxides of phosphorus are—

(i) **Phosphorus trioxide** (P_2O_3 or P_4O_6).

(ii) **Phosphorus pentoxide** (P_2O_5 or P_4O_{10}).

5.12. Phosphorus trioxide (P_2O_3 or P_4O_6)—anhydride of phosphorus acid.

- **Preparation :** Phosphorus trioxide is prepared by burning *white phosphorus* in a *limited supply of air*.

$$P_4 + 3O_2 = 2P_2O_3$$

Pieces of white phosphorus are taken in a glass tube clamped horizontally to a stand. One end of the glass tube is connected to a condenser. The other end of the condenser is connected to a U-tube. At the bottom of the U-tube there is a glass bottle which is placed in a freezing mixture. A plug of glass wool is inserted into the inner tube of the condenser near its exit. Warm water at 50°C—60°C is passed through the outer jacket of the condenser. A slow current of air is passed over the pieces of white phosphorus. As soon as the white phosphorus of the glass tube comes in contact with air it burns and is oxidised to produce phosphorus trioxide along with small amount of phosphorus pentoxide. The vapours of these two oxides pass through the condenser when the vapours of phosphorus pentoxide are arrested by the plug of the glass wool and the vapours of phosphorus trioxide pass out and condense to a solid mass in the cooled bottle under the U-tube. Phosphorus trioxide thus obtained is purified by distilling it in inert atmosphere.

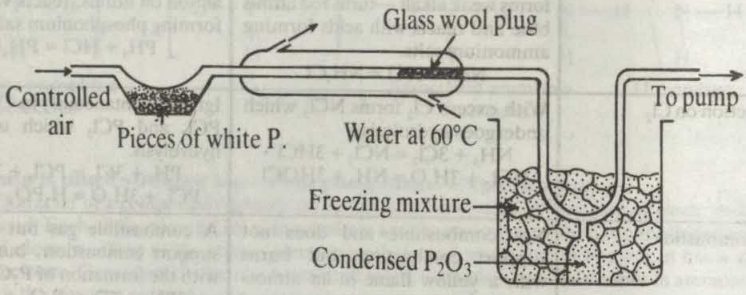


Fig 5.10 : Preparation of phosphorus trioxide

- **Property : Physical :** At ordinary temperature P_2O_3 is white, crystalline and waxy solid. Its melting point is 23·8°C. It is soluble in water and in organic solvents like benzene, ether, CS_2 etc. It inflames in contact with alcohol. It has a smell like that of garlic.

Chemical : (i) (a) P_2O_3 is an *acidic oxide*. It dissolves in cold water to produce *phosphorus acid*.

$$P_2O_3 + 3H_2O = 2H_3PO_3$$

(b) With *hot water* it yields *phosphine* and phosphoric *acid*.

$$2P_2O_3 + 6H_2O = PH_3 + 3H_3PO_4$$

(ii) *Oxidation :* Phosphorus trioxide is readily oxidised by air or oxygen to *phosphorus pentoxide*.

$$P_2O_3 + O_2 = P_2O_5$$

(iii) *Decomposition* : P_2O_3 decomposes at 400°C to give *phosphorus dioxide* and *red phosphorus.*

$$2P_2O_3 = 3PO_2 + P(\text{red})$$

- **Uses** : It is used in the preparation of phosphorus acid.
- **Structure** : From the vapour density measurement it has been found that the molecular formula of phosphorus trioxide is P_4O_6. In its molecule the 4 P-atoms are situated at the 4 corners of a tetrahedron. Each of the six oxygen atoms is linked to two P atoms by single covalent bond by the formation of six non linear P—O—P arrangements. Thus by such arrangements all the 4 P-atoms and 6 oxygen atoms are in a position to complete their electron octets. The P—P bonds are absent in this structure. An unused electron pair (lone pair) is left on each P-atom.

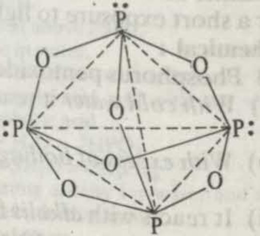


Fig 5.11 : Structure of P_4O_6

5.13. Phosphorus pentoxide [P_2O_5 or P_4O_{10}].

- **Preparation :**

(i) **By the oxidation of phosphorus :**

Phosphorus pentoxide is prepared when white or red phosphorus is burnt in excess of air or oxygen.

$$P_4 + 5O_2 = P_4O_{10}$$

Pieces of white phosphorus are placed in iron crucible resting on a tile. The phosphorus is then ignited by touching it with a hot iron wire and immediately covered with a bell jar. Phosphorus burns in the bell jar and is oxidised by the air inside the bell jar to produce white clouds of phosphorus pentoxide. The bell jar lifted slightly from time to time to admit fresh air inside the jar to complete the oxidation. After the completion of the reaction the bell jar is cooled. The white clouds of phosphorus pentoxide gradually settle down as snowy white soft powder.

The phosphorus pentoxide thus produced contains P_2O_3 in small quantity. It is sublimated in a current of dry ozonised air over platinised asbestos, when the P_2O_3 present is oxidised to P_2O_5 and the sublimate is collected in a cooled receiver.

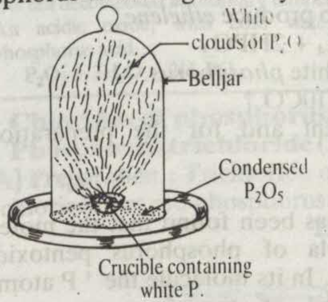


Fig 5.12 : Preparation of phosphorus pentoxide

(ii) **Phosphorus pentoxide from orthophosphoric acid :**

Phosphorus pentoxide can be obtained by heating orthophosphoric acid at an elevated temperature. At 213°C orthophosphoric acid is converted to *pyrophosphoric acid.* At 316°C the pyrophosphoric acid transformed into *metaphosphoric acid.* At higher temperature metaphosphoric acid is converted to *phosphorus pentoxide* on dehydration.

$$2H_3PO_4 \xrightarrow{213^\circ C} \underset{(\text{Pyrophosphoric})}{H_4P_2O_7} + H_2O\uparrow$$

$$H_4P_2O_7 \xrightarrow{316^\circ C} \underset{(\text{Metaphosphoric})}{2HPO_3} + H_2O\uparrow$$

$$2HPO_3 \xrightarrow{600\text{—}700^\circ C} P_2O_5 + H_2O\uparrow$$

(iii) *White phosphorus* on being heated with *carbon di-oxide at 1000°C* yields phosphorus pentoxide.

$$2P + 5CO_2 = P_2O_5 + 5CO \uparrow$$

- **Properties of phosphorus pentoxide :**

Physical : At an ordinary temperature P_2O_5 is a soft white powder. It becomes crystalline like snow when cooled. It sublimes at 250°C. It exhibits phosphorescence after a short exposure to light especially at low temperatures.

Chemical :

(i) Phosphorus pentoxide is an *acidic oxide.*

(a) *With cold water* it reacts with a hissing sound to yield *metaphosphoric acid.*

$$P_2O_5 + H_2O = 2HPO_3$$

(b) *With excess of boiling water* it gives *orthophosphoric acid.*

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

(ii) It reacts with *alkalis* forming *phosphates* and *metaphosphates.*

$$6NaOH + P_2O_5 = 2Na_3PO_4 + 3H_2O$$
$$2NaOH + P_2O_5 = 2NaPO_3 + H_2O$$

(iii) Phosphorus pentoxide has a great affinity for water. It is a strong drying agent because of its power to abstract the elements of water from other compounds. Thus, it can dehydrate conc. H_2SO_4, HNO_3 and $HClO_4$ yielding SO_3, N_2O_5 and Cl_2O_7 respectively and P_2O_5 itself being converted to *metaphosphoric acid.*

$$H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$$
$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$$
$$2HClO_4 + P_2O_5 = Cl_2O_7 + 2HPO_3$$

Thus SO_3, N_2O_5 and Cl_2O_7 are the anhydrides of H_2SO_4, HNO_3 and $HClO_4$ respectively. P_2O_5 can dehydrate *ethyl alcohol* to produce *ethelene.*

$$C_2H_5OH + P_2O_5 = C_2H_4 + 2HPO_3$$

(iv) At 1500°C it is reduced by *coke* to give white *phosphorus.*

$$2P_2O_5 + 10C = P_4 + 10CO \uparrow$$

- **Uses :** It is used as dehydrating agent and for the preparation of orthophosphoric acid, N_2O_5 and SO_3.

- **Structure of phosphorus pentoxide :**

From the vapour density measurement, it has been found that the molecular formula of phosphorus pentoxide is P_4O_{10}. In its molecule the 4 P atoms are situated at the four corners of a tetrahedron. Each of the six oxygen atoms is linked to two P-atoms by single covalent bond by the formation of six non linear P—O—P arrangements, and each of the four oxygen atoms is linked to each P-atom by co-ordination bond.

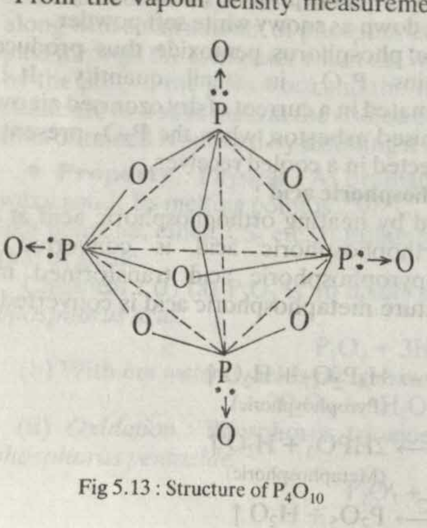
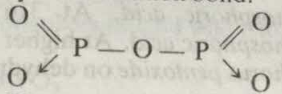
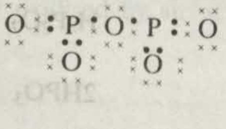


Fig 5.13 : Structure of P_4O_{10}



Electron dot structure of P_2O_5

or



• Comparison between P_2O_3 and P_2O_5 •

Phosphorus trioxide (P_2O_3)	Phosphorus pentoxide (P_2O_5)
(1) At ordinary temperature it is white crystalline waxy solid.	(1) At ordinary temperature it is soft white powder —becomes crystalline like snow when cooled.
(2) It has a smell like that of garlic.	(2) It is odourless.
(3) Its m.p. is 23·8°C.	(3) It sublimes at above 250°C.
(4) It is soluble in water and in organic solvents.	(4) It is soluble in water.
(5) It is an acidic oxide—with cold water it gives phosphorus acid and with hot water it gives phosphoric acid and phosphine. $P_2O_3 + 3H_2O = 2H_3PO_3$ $2P_2O_3 + 6H_2O = PH_3 + 3H_3PO_4$	(5) It is an acidic oxide—with cold water it gives metaphosphoric acid and with hot water it gives phosphoric acid. $P_2O_5 + H_2O = 2HPO_3$ $P_2O_5 + 3H_2O = 2H_3PO_4$
(6) It can not absorb water and so it is not dehydrating agent.	(6) It has a strong affinity for water and so it is used as a dehydrating agent.
(7) It is highly poisonous.	(7) It is not poisonous.
(8) It is oxidised to P_2O_5 when exposed to air or oxygen.	(8) It is not oxidised by air or oxygen.

• Comparison between P_2O_3 and N_2O_3 •

Phosphorus trioxide (P_2O_3)	Dinitrogen trioxide (N_2O_3)
(1) White crystalline waxy solid having low melting point.	(1) At ordinary temperature it is a brown gas.
(2) Highly poisonous.	(2) Not so poisonous.
(3) Has a smell like that of gralic.	(3) Has a smell like that of nitric acid.
(4) It is not decomposed at ordinary temperatures.	(4) Decomposes at ordinary temperatures.
(5) An acidic oxide, with cold water gives phosphorus acid. $P_2O_3 + 3H_2O = 2H_3PO_3$	(5) An acidic oxide, gives nitrous acid with water. $N_2O_3 + H_2O = 2HNO_2$

• Chlorides of phosphorus.

1. Phosphorus trichloride (PCl_3) :

[A] Preparation : Trichloride of phosphorus is prepared by passing a current of dry chlorine over red phosphorus.

$$2P + 3Cl_2 = 2PCl_3$$

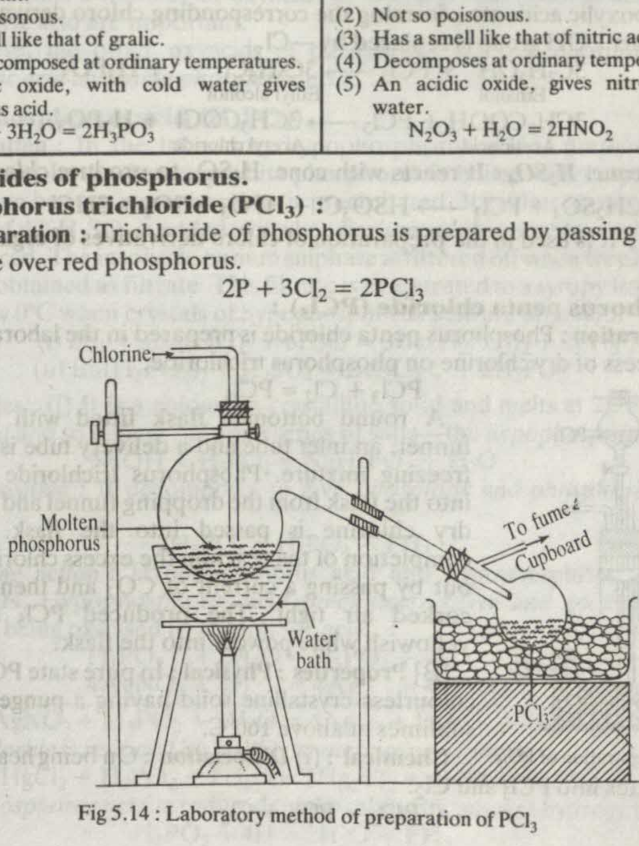


Fig 5.14 : Laboratory method of preparation of PCl_3

Red phosphorus is taken in a retort and is heated gently on a water bath—the air inside the retort being previously replaced by CO_2. The phosphorus trichloride thus produced distills over and collects in a receiver kept in freezing mixture.

The product thus obtained may contain some phosphorus pentachloride. To remove the PCl_5, the product is distilled with white phosphorus when pure PCl_3 is obtained as distillate.

$$3PCl_5 + 2P = 5PCl_3$$

[B] **Properties : Physical :** Phosphorus trichloride is a colourless liquid having a pungent smell. Its boiling point is 76°C and sp. gr = 1·57. It fumes in air.

Chemical : (i) ***Hydrolysis* :** PCl_3 is hydrolysed by cold water with the formation of *phosphorus acid* and *hydrogen chloride.* It fumes strongly in moist air because of the formation of hydrogen chloride by hydrolysis. Due to the pressure of HCl the aqueous solution of PCl_3 can conduct electricity.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

(ii) ***With chlorine* :** It combines with chlorine to form phosphorus pentachloride.

$$PCl_3 + Cl_2 = PCl_5$$

(iii) ***With sulphur trioxide* :** It reacts with sulphur trioxide to produce phosphorus oxy chloride and SO_2.

$$SO_3 + PCl_3 = POCl_3 + SO_2$$

(iv) ***Replacement of (−OH) group by (−Cl) in organic compounds.***

It reacts with many organic compounds having hydroxyl group (−OH), e.g., alcohol, carboxylic acids etc., forming the corresponding chloro derivatives. In all these reactions −OH group is replaced by —Cl.

$$3\underset{\text{Ethanol}}{C_2H_5OH} + PCl_3 \longrightarrow 3\underset{\text{Ethyl alcohol}}{C_2H_5Cl} + H_3PO_3$$

$$3\underset{\text{Acetic acid}}{CH_3COOH} + PCl_3 \longrightarrow 3\underset{\text{Acetyl chloride}}{CH_3COCl} + H_3PO_3$$

(v) ***With conc. H_2SO_4* :** It reacts with conc. H_2SO_4 to produce *chlorosulphonic acid.*

$$2H_2SO_4 + PCl_3 \longrightarrow HSO_3Cl + HPO_3 + SO_2 + 2HCl$$

[C] **Uses :** It is used in the preparation of chloro derivatives of organic hydroxy compounds.

2. Phosphorus penta chloride (PCl_5) :

[A] **Preparation :** Phosphorus penta chloride is prepared in the laboratory by the action of excess of dry chlorine on phosphorus trichloride.

$$PCl_3 + Cl_2 = PCl_5$$

A round bottomed flask fitted with a dropping funnel, an inlet tube and a delivery tube is cooled in a freezing mixture. Phosphorus trichloride is dropped into the flask from the dropping funnel and a current of dry chlorine is passed into the flask. After the completion of the reaction the excess chlorine is driven out by passing a current of CO_2 and then the flask is corked air tight. The produced PCl_5 deposits as yellowish white powder into the flask.

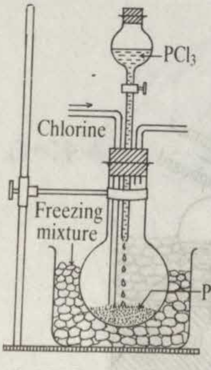


Fig 5. 15 : Preparation of PCl_5

[B] **Properties : Physical :** In pure state PCl_5 is almost colourless crystalline solid having a pungent smell. It sublimes at above 160°C.

Chemical : (i) ***Dissociation* :** On being heated strongly PCl_5 dissociates into PCl_3 and Cl_2.

$$PCl_5 = PCl_3 + Cl_2$$

(ii) ***Hydrolysis*** : It combines with a limited amount of water yielding *phosphorus oxychloride* and *hydrogen chloride.* With excess of water it is completely hydrolysed to give *phosphoric acid.*

$$PCl_5 + H_2O = POCl_3 + 2HCl$$
$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

Phosphorus pentachloride *fumes in moist air due to* the production of *hydrogen chloride* by hydrolysis.

(iii) ***With sulphur dioxide,*** phosphorus penta chloride replaces one oxygen atom of SO_2 by two Cl atoms yielding *thionyl chloride.*

$$SO_2 + PCl_5 = SOCl_2 + POCl_3$$

(iv) ***Replacement of (−OH) group of organic compounds by (−Cl)*** : Phosphorus pentachloride replaces the hydroxyl group of many organic and inorganic compounds by −Cl. It reacts with ethyl alcohol producing ethyl chloride.

$$\begin{array}{lllll} C_2H_5OH & + PCl_5 & \rightarrow C_2H_5Cl & + POCl_3 & + HCl \\ CH_3COOH & + PCl_5 & \rightarrow CH_3COCl & + POCl_3 & + HCl \\ \underset{\text{Sulphuric acid}}{OH.SO_2OH} & + 2PCl_5 & \rightarrow SO_2Cl_2 & + 2POCl_3 & + 2HCl \end{array}$$

[C] **Uses** : PCl_5 is used in organic synthesis to replace −OH group by −Cl group.

5.14. Oxyacids of phosphorus.

Phosphorus forms a number of oxyacids of which (i) *Phosphorus acid* and (ii) *ortho phosphoric* acid are important.

Besides these, the other oxyacids of phosphorus are *hypophosphorus acid, pyrophosphoric acid* and *meta phosphoric acid.*

1. Hypophosphorus acid (H_3PO_2).

[A] **Preparation** : In the laboratory hypophosphorus acid is prepared by the following process. In the first step white phosphorus is boiled with *baryta solution* $[Ba(OH)_2]$ when barium hypophosphite is precipitated. It is filtered out and calculated amount of dil. H_2SO_4 is added to it when *barium sulphate* and *hypophosphorus acid* are produced. The insoluble barium sulphate is filtered off when free hypophosphorus acid is obtained as filtrate. This filtrate is evaporated to a syrupy liquid which is cooled below 0°C when crystals of hypophosphorus acid are obtained.

$$\text{(i) } 2P_4 + 3Ba(OH)_2 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3\uparrow$$
$$\text{(ii) } Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4\downarrow + 2H_3PO_2$$

[B] **Properties** : (i) It is a colourless crystalline solid and melts at 26·5°C. It is a *monobasic acid* and so it gives only one series of salts—the *hypophosphites.*

$$NaOH + H_3PO_2 = NaH_2PO_2 + H_2O$$

(ii) ***Decomposition*** : It decomposes to give *phosphine and phosphoric acid* on strong heating.

$$2H_3PO_2 = H_3PO_4 + PH_3$$

(iii) ***Reducing action*** : Hypophosphorus acid and hypophosphites are strong reducing agents. Hypophosphorus acid *precipitates silver and gold* from their solutions itself being oxidised to phosphoric acid.

$$\begin{array}{l} H_3PO_2 \quad + 2H_2O = H_3PO_4 + 4H \\ 4AgNO_3 + 4H \quad = 4Ag \quad + 4HNO_3 \\ \hline 4AgNO_3 + H_3PO_2 + 2H_2O = 4Ag\downarrow + H_3PO_4 + 4HNO_3 \end{array}$$

Mercuric chloride is reduced by H_3PO_2 to *mercurous chloride.*

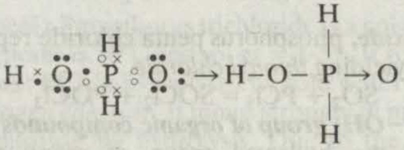
$$4HgCl_2 + H_3PO_2 + 2H_2O = 2Hg_2Cl_2 + 4HCl + H_3PO_4$$

(iv) *Hypophosphorus acid* is reduced to *phosphine* by nascent hydrogen.

$$H_3PO_2 + 4H = 2H_2O + PH_3$$

[C] **Uses** : Some of its salts are used in medicine as nerve tonic.

- **Structure of hypophosphorus acid :** Inspite of the presence of three H-atoms in hypophosphorus acid, it is monobasic as it has only one replaceable H-atom. Two others are linked directly to the P-atom by covalent bond. Thus the acid has the following structure.

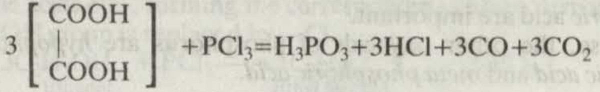


$$H \times \ddot{\underset{\cdot\cdot}{O}} : \overset{H}{\underset{H}{P}} : \ddot{\underset{\cdot\cdot}{O}} : \rightarrow H-O-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{P}} \rightarrow O$$

2. Phosphorus acid (H_3PO_3).

[A] **Preparation :** (1) *By the hydrolysis of PCl_3 :* Phosphorus acid is prepared by dissolving PCl_3 in cold water when PCl_3 undergoes hydrolysis yielding phosphorus acid. $PCl_3+3H_2O=H_3PO_3+3HCl$. The aqueous solution thus obtained is evaporated at 180°C when HCl present in the solution is removed. The solution on being cooled yields crystals of phosphorus acid.

(ii) *By the action of oxalic acid on PCl_3 :* A *mixture of oxalic acid* and *phosphorus trichloride* on being heated yields phosphorus acid.



$$3\begin{bmatrix} COOH \\ | \\ COOH \end{bmatrix} + PCl_3 = H_3PO_3 + 3HCl + 3CO + 3CO_2$$

[B] **Properties :** Phosphorus acid is white crystalline solid. It is hygroscopic substance. Its m.p. is 74°C.

(i) ***Decomposition*** : Crystals of phosphorus acid on being heated at 300°C, decompose to give phosphine and ortho-phosphoric acid. In this reaction H_3PO_3 is reduced to phosphine and at the same time it is *oxidised to phosphoric acid*. This type of redox reaction is known as *disproportionation*.

$$4H_3\overset{+3}{P}O_3 = 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$$

(ii) ***Oxidation*** : It is slowly oxidised by the atmospheric oxygen to form *phosphoric acid*.

$$2H_3PO_3 + O_2 = 2H_3PO_4$$

(iii) H_3PO_3 in its aqueous solution behaves as a *dibasic acid*. Inspite of the presence of 3 H-atoms in its molecule, only 2 of them are replaceable.

$$H_3PO_3 \rightleftharpoons 2H^+ + HPO_3^{--}$$

As a result two series of salts are given by H_3PO_3 e.g., *sodium dihydrogen phosphite* NaH_2PO_3 and *disodium hydrogen phosphite* (Na_2HPO_3). The third H-atom is non-replaceable, consequently no salt such as Na_3PO_3 is known.

Na_2HPO_3, though looks like an acid salt, it is actually a normal salt as there is no replaceable H-atom in it.

(iv) *It reacts with PCl_5* with the formation of PCl_3 and $POCl_3$.

$$H_3PO_3 + 3PCl_5 = PCl_3 + 3POCl_3 + 3HCl$$

(v) ***Reducing action*** : Phosphorus acid is a strong reducing agent.

(a) It reduces *mercuric chloride* to *mercurous chloride*.

$$2\overset{+2}{Hg}Cl_2 + H_3PO_3 + H_2O = \overset{+1}{Hg_2}Cl_2 + 2HCl + H_3PO_4$$

(b) H_3PO_3 reduces *copper sulphate solution* to *metallic copper* and *silver nitrate solution* to *metallic silver*.

$$\overset{+2}{CuSO_4} + \overset{+3}{H_3PO_3} + H_2O = \overset{0}{Cu} + H_2SO_4 + \overset{+5}{H_3PO_4}$$
$$2AgNO_3 + H_3PO_3 + H_2O = 2Ag + 2HNO_3 + H_3PO_4$$

(c) It declourises the pink colour of *acidified potassium permanganate* solution reducing it to colourless *manganous salt*.

$$\begin{gathered} 2KMnO_4 = K_2O + 2MnO + 5O \\ 5H_3PO_3 + 5O = 5H_3PO_4 \\ K_2O + H_2SO_4 = K_2SO_4 + H_2O \\ 2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O \\ \hline 2K\overset{+7}{Mn}O_4 + 5H_3\overset{+3}{P}O_3 + 3H_2SO_4 = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 5H_3\overset{+5}{P}O_4 + 3H_2O \end{gathered}$$

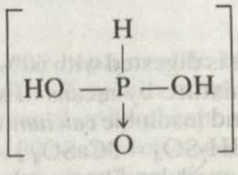
(d) H_3PO_3 reduces sulphur dioxide to sulphur.

$$\overset{+4}{S}O_2 + 2H_3PO_3 = \overset{0}{S} + 2H_3PO_4$$

(e) It reduces iodine to hydroiodic acid.

$$\overset{0}{I_2} + H_3PO_3 + H_2O = 2H\overset{-1}{I} + H_3PO_4$$

[C] **Molecular structure :** The molecular formula of phosphorus acid is H_3PO_3. In its molecule two $-OH$ groups are attached to P-atom by covalent bond. One H atom is directly linked to P-atom by covalent bond and 1 oxygen atom is joined to p-atom by coordinate bond.



$$\left[\begin{array}{c} H \\ | \\ HO - P - OH \\ \downarrow \\ O \end{array}\right].$$

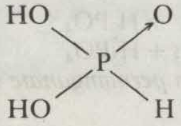
• Phosphorus acid is a strong reducing agent.—Explain why.

The P-atom in H_3PO_3 is in (+3) oxidation state. The next higher oxidation state of phosphorus is (+5) as in H_3PO_4. So the P-atom in H_3PO_3 has an inherent tendency to go to (+5) oxidation stated from (+3). Thus the P-atom in H_3PO_3 is oxidised by increasing its oxidation number from (+3) to (+5) This oxidation is carried out by reducing the other substances. Thus H_3PO_3 exhibits reducing property. As for example, it reduces $CuSO_4$ to metallic Cu, itself being oxidised to H_3PO_4.

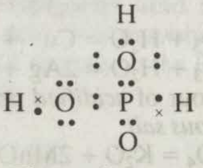
$$\overset{+2}{Cu}SO_4 + H_3\overset{+3}{P}O_3 + H_2O = \overset{0}{Cu} + H_3\overset{+5}{P}O_4 + H_2SO_4$$

• Although the formula of phosphorus acid is H_3PO_3, it is actually a dibasic acid, or, Na_2HPO_3 is a normal salt, or, no salt such as Na_3PO_3 is known—Explain why.

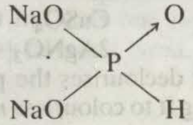
In the molecule of phosphorus acid, out of the 3 H-atoms, one hydrogen atom is directly linked to the P-atom by single covalent bond. The two other H-atoms are joined to the P-atom through two oxygen atoms forming two hydroxyl groups. The two H-atoms of the two OH groups are replaceable and only these two H-atoms take part in forming salts. The other H-atom which is directly linked to the P-atom, cannot be replaced by any metallic radical. Thus H_3PO_3 is a dibasic acid inspite of the presence of three H-atoms in its molecule. For this reason $Na_2H\ PO_3$ is not an acid salt but a normal salt, as the H-atom present in it is directly linked to the P-atom by single covalent bond and so this H-atom is non-replaceable. In H_3PO_3 only two H-atom are replaceable. These two H-atoms can be replaced by metallic radical to form salts, but the third H-atom is not replaceable. Consequently the salt of the type Na_3PO_3 does not exist at all.



Molecular structure of H_3PO_3



Electron dot structure of H_3PO_3



Molecular structure of Na_2HPO_3

3. Ortho phosphoric acid (H_3PO_4).

[A] Preparation of ortho phosphoric acid.

(i) By the action of conc. HNO_3 and phosphorus.

In the laboratory ortho phosphoric acid is prepared by the action of *concentrated nitric acid* or *red phosphorus*.

$$4P + 10\,HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2$$

Red phosphorus and conc. HNO_3 are taken in a flask and the mixture is heated when ortho phosphoric acid along with nitric oxide and nitrogen dioxide are produced. After the completion of the reaction the resulting solution is heated to 180°C when the oxides of nitrogen are removed and a concentrated solution of ortho phosphoric acid is obtained. This concentrated solution of phosphoric acid is placed in a vacuum desiccator which is kept immersed in a freezing mixture, when colourless crystals of ortho phosphoric acid are obtained.

(ii) From bone ash :

Bone ash or *mineral phosphate* is digested with 60% sulphuric acid in a lead lined cast iron tank, by heating the mixture by means of steam. On completion of the reaction *ortho phosphoric acid* and insoluble *calcium sulphate* are produced.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4\downarrow + 2H_3PO_4$$

The calcium sulphate is removed by filtering the mixture through a bed of powdered coke. The filtrate is evaporated to obtain syrupy ortho phosphoric acid.

(iii) *Phosphoric acid may also be obtained on a large scale* by heating a mixture of *powdered mineral phosphate, silica* and *coke* in an electric furnace.

At 1200°C, $Ca_3(PO_4)_2$ reacts with silica to form P_2O_5 and at 1500°C the produced P_2O_5 is reduced by coke to form white phosphorus and CO. The vapours of white phosphorus along with carbon monoxide are mixed with a current of air when white phosphorus is oxidised to give P_2O_5 and CO is oxidised to CO_2. The produced P_2O_5 on being reacted with boiling water yields ortho phosphoric acid.

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$$

$$2P_2O_5 + 10C = P_4 + 10CO$$

$$P_4 + 5O_2 = 2P_2O_5$$

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

[B] Properties of ortho phosphoric acid.

Physical : Ortho phosphoric acid is a glassy crystalline solid. Its melting point is 42°C. The crystals of orthophosphoric acid absorb moistures from air producing a syrupy liquid. It is highly soluble in water.

Chemical :

(i) ***Action of heat :***

(a) On being heated to 213°C, phosphoric acid loses elements of water from its molecule and is converted to *pyro phosphoric acid*.

$$2H_3PO_4 \overset{213°C}{\rightleftharpoons} H_2O + \underset{\text{Pyrophosphoric}}{H_4P_2O_7}$$

(b) When pyrophosphoric acid is heated further to 315°C, it is converted to *meta phosphoric acid.*

$$H_4P_2O_7 \rightleftharpoons 2HPO_3 + H_2O$$

(c) At 600°C—700°C meta phosphoric acid decomposes to give *phosphorus pentoxide.*

$$2HPO_3 \rightleftharpoons P_2O_5 + H_2O$$

(ii) ***Acid property :*** Phosphoric acid is a *tribasic acid* as all the three H-atoms in its molecule are replaceable. Consequently it produces three series of salts by its action on alkalis. These salts are called *phosphates.*

(a) By the replacement of one H-atom from H_3PO_4 by metallic radical, *primary phosphates* or *acid phosphates* are produced e.g., *sodium dihydrogen phosphate* (NaH_2PO_4).

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

(b) By the replacement of 2 H-atoms by metallic radicals, *secondary phosphates* are produced, e.g., *di-sodium hydrogen phosphate* (Na_2HPO_4).

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$$

(c) *Tertiary phosphates* are formed by the replacement of 3 H-atoms by metallic radicals, e.g., *sodium phosphate* (Na_3PO_4).

$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$$

The *aqueous solution of tertiary phosphates* are *alkaline in nature* due to hydrolysis.

• Inspite of the presence of 3 replaceable H-atoms ortho phosphoric acid behaves as a dibasic acid—Explain why.

Although the molecular structure of ortho phosphoric acid shows the presence of three $-OH$ groups, it behaves as a dibasic acid in its solution. The different dissociation constants (K) of H_3PO_4 and the corresponding *pK* values are given below—

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad (K_1 = 7.5\times10^{-3}),\ pK_1 = -\log 7.5\times10^{-3} = 2.12$$
$$H_2PO_4 \rightleftharpoons H^+ + H_2PO_4^{2-} \quad (K_2 = 6.3\times10^{-8}),\ pK_2 = -\log 6.3\times10^{-8} = 7.21$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \quad (K_3 = 2.2\times10^{-13}),\ pK_3 = -\log 2.2\times10^{-13} = 12.67$$

(i) On titration with NaOH solution phosphoric acid *behaves as monobasic acid* with *methyl orange at the stage of NaH_2PO_4.*

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

The pH at the equivalence point = $1/2pk_1 + 1/2pk_2 = 1/2\times2.12 + 1/2\times7.21 = 4.66$, which is very close to the range of methyl orange.

(ii) *It is dibasic with phenolphthalein at the stage of Na_2HPO_4.*

$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$$

The pH at the equivalence point = $1/2pk_2 + 1/2pk_3 = 1/2\times7.21 + 1/2\times12.67 = 9.94$, which is very close to the range of phenolphthalein.

(iii) *Direct titration of phosphoric acid as a tribasic acid is not possible with any indicator, as the third dissociation constant of H_3PO_4 is very small.* Hence the reaction $H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$, does not take place in aqueous medium. This explains why H_3PO_4 behaves as dibasic acid in aqueous medium inspite of the presence of three OH groups in its molecule.

However, the indirect titrations of H_3PO_4 shows that it is tribasic. To a known volume of H_3PO_4 excess of $CaCl_2$ solution is added when a white precipitate of

$Ca_3(PO_4)_2$ is formed. The filtrate contains HCl, which is titrated by NaOH solution using phenolpthalein indicator.

$$2H_3PO_4 + 3CaCl_2 = Ca_3(PO_4)_2\downarrow + 6HCl$$
$$6HCl + 6NaOH = 6NaCl + 6H_2O$$

(iv) ***Action on silver nitrate :*** *A yellow precipitate* of *silver phosphate* is obtained when H_3PO_4 is treated with $AgNO_3$ solution.

$$3AgNO_3 + H_3PO_4 = Ag_3PO_4\downarrow + 3HNO_3$$

(v) ***Action on $BaCl_2$:*** Barium chloride gives a white precipitate of *barium ortho phosphate* in *neutral* or *slightly alkaline solution.*

$$3BaCl_2 + 2H_3PO_4 = Ba_3(PO_4)_2\downarrow + 6HCl$$

(vi) ***Action on bromides or iodides :*** Phosphoric acid reacts with *bromide* or *iodide salts* yielding HBr and HI respectively.

$$3NaBr + H_3PO_4 = Na_3PO_4 + 3HBr$$

(vii) ***Action on magnesium salts :*** Phosphoric acid reacts with magnesium salts in presence of *ammonium chloride* and *ammonium hydroxide* yielding a *white crystalline precipitate* of *ammonium magnesium phosphate.*

$$H_3PO_4 + MgCl_2 + 3NH_4OH + 3H_2O = NH_4MgPO_4,6H_2O\downarrow + 2NH_4Cl$$

- **Identification of phosphoric acid and phosphates :**

(i) *Phosphoric acid* or *phosphates* on being treated with *conc. HNO_3* and *ammonium molybdate* solution yields a *light yellow precipitate of ammonium phospho molybdate.*

$$Na_2HPO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 = (NH_4)_3\,[PMo_{12}O_{40}] + 2NaNO_3 + 21NH_4NO_3 + 12H_2O$$

(ii) Phosphoric acid or the solution of phosphates on being treated with $MgCl_2$ in presence NH_4Cl and NH_4OH yields a *crystalline white precipitate* of *ammonium magnesium phosphate.*

$$H_3PO_4 + MgCl_2 + 3NH_4OH + 3H_2O = NH_4MgPO_4,6H_2O\downarrow + 2NH_4Cl$$

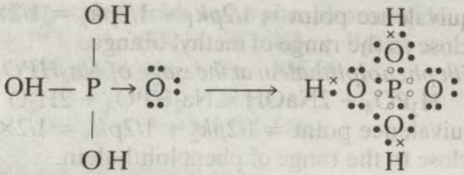
- **Uses of phosphoric acid :**

Phosphoric acid is used,

(i) in the preparation of HBr and HI in the laboratory,
(ii) as a stabilizer for hydrogen peroxide,
(iii) in the manufacture of fertilizers, dyes, enamels etc.,
(iv) in the preparation of nerve tonic in medicine.

- **Structure :**

Phosphoric acid is tribasic, so it must contain three OH groups in its molecule which are directly attached to the P-atom.



- **Prove that ortho phosphoric acid and phosphorus acid contain phosphorus :**

Phosphorus acid is heated strongly when it decomposes to give orthophosphoric acid and phosphine.

$$4H_3PO_3 = PH_3 + 3H_3PO_4$$

The ortho phosphoric acid thus obtained is mixed with powdered charcoal and the mixture is dried in an iron vessel by applying heat. The dried mass is taken in a retort and heated strongly and the evolved vapours are passed through cold water. As a result a white residue is found to collect under water. This residue burns spontaneously when comes in contact with air producing white smoke. It dissolves in CS_2 and emits phosphorescence. Thus it is proved that the white residue is phosphorus and this phosphorus has come from phosphorus acid and phosphoric acids.

$$H_3PO_4 \xrightarrow{heat} HPO_3 + H_2O, \qquad 4HPO_3 + 12C = 2H_2 + 12CO + P_4$$

• Comparison between phosphorus acid and phosphoric acid. •

Phosphorus acid (H_3PO_3)	Phosphoric acid (H_3PO_4)
(1) Phosphorus acid is white crystalline deliquescent solid.	(1) Phosphoric acid is colourless, crystalline extremly deliquescent.
(2) Melting point = 74°C.	(2) Melting point = 42°C.
(3) Inspite of the presence of 3 H-atoms in its molecule, it is dibasic and forms two series of salts e.g., Na_2HPO_4 (normal) and NaH_2PO_4 (acid salt).	(3) It is tribasic and so it forms three series of salts e.g., NaH_2PO_4 (Primary), Na_2HPO_4 (secondary) and Na_3PO_4 (tertiary).
(4) On being heated strongly it decomposes to to give phosphine and phosphoric acid. $4H_3PO_3 = 3H_3PO_4 + PH_3$	(4) On gradual heating it loses water and is converted first into pyrophosphoric acid, then meta phosphoric and finally to P_2O_5. $2H_3PO_4 \rightarrow H_4P_2O_7 \rightarrow 2HPO_3 \rightarrow P_2O_5$
(5) Phosphorus acid is a strong reducing agent. It reduces $CuSO_4$ solution to metallic Cu and $AgNO_3$ solution to metallic silver. $CuSO_4 + H_3PO_3 + H_2O = Cu\downarrow + H_2SO_4 + H_3PO_4$	(5) As the P-atom in H_3PO_4 is in its highest oxidation state (+5), it has no scope to be oxidised and hence it can not reduce other substances, i.e., it can not act as a reducing agent.

4. Pyrophosphoric acid $H_4P_2O_7$:

Preparation : (i) Pyrophosphoric acid is prepared in the laboratory by heating orthophosphoric acid between 200°C to 300°C.

$$2H_3PO_4 \xrightarrow[\Delta]{} H_4P_2O_7 + H_2O$$

Properties : (i) It is white crystalline solid which melts at 61°C. It is soluble in water.

(ii) ***Action on alkalis :*** It is tetrabasic acid but it forms only two series of salts when it is reacted with alkalis.

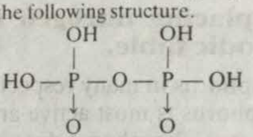
$$\underset{}{2NaOH + H_4P_2O_7} = \underset{\substack{\text{Disodium acid}\\\text{Pyrophosphate}}}{Na_2H_2P_2O_7} + 2H_2O.$$

$$4NaOH + H_4P_2O_7 = \underset{\substack{\text{Tetrasodium neutral}\\\text{Pyrophosphate}}}{Na_4P_2O_7} + 4H_2O.$$

(iii) ***Action of water :*** In aqueous solution it is slowly converted to orthophosphoric acid and the conversion is rapid if the solution is boiled.

$$H_4P_2O_7 + H_2O = 2H_3PO_4$$

Structure : As $H_4P_2O_7$ is tetrabasic acid, the two (–OH) groups are linked to each of the two P-atoms present in its molecule. Hence it has the following structure.



5. Metaphosphoric acid (HPO_3) :

Preparation : (i) Metaphosphoric acid is prepared by dissolving phosphorus pentoxide in a limited amount of cold water.

$$P_2O_5 + H_2O = 2HPO_3$$

(ii) It can also be prepared by heating ammonium phosphate or phosphoric acid to above 400°C.

$$(NH_4)_3PO_4 \xrightarrow[\Delta]{} HPO_3 + 3NH_3 + H_2O.$$

$$H_3PO_4 \xrightarrow[\Delta]{} HPO_3 + H_2O.$$

Properties : (i) Pure acid is transparent deliquescent solid. It is very poisonous.

(ii) ***Action of water :*** It is readily soluble in water and its aqueous solution slowly changes to orthophosphoric acid. This conversion is rapid in presence of acids and on boiling.

$$HPO_3 + H_2O = H_3PO_4$$

(iii) ***With barium chloride :*** It gives a white precipitate of *barium meta phosphate* in neutral or alkaline solution of $BaCl_2$.

$$BaCl_2 + 2HPO_3 = Ba(PO_3)_2 + 2HCl$$

(iv) Metaphosphoric acid reacts with *silver nitrate* solution yielding a white precipitate of silver metaphosphate.

$$AgNO_3 + HPO_3 = AgPO_3\downarrow + HNO_3$$

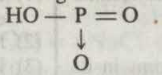
(v) Alkali metaphosphates on being heated with metallic oxides produce mixed phosphates.

$$NaPO_3 + CuO = NaCuPO_4$$

(vi) Metaphosphoric acid is a monobasic acid and is moderately strong. Its salts are known as metaphosphates. These salts give rise to polymers of the type $(NaPO_3)_n$.

Uses : *Sodium hexa meta phosphate* is extensively used for softening hard water.

Structure : As it is monobasic it has the following structure.



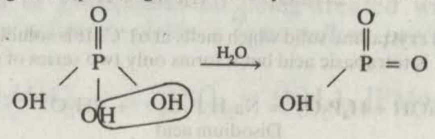
$$HO - \underset{\underset{O}{\downarrow}}{P} = O$$

• Distinguishing tests for ortho, meta and pyro phosphoric acid •

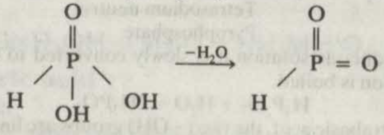
Reaction	Ortho-phosphoric acid	Pyro-phosphoric acid	Meta-phosphoric acid
1. Neutral silver nitrate solution.	Yellow ppt. of Ag_3PO_4.	White crystalline ppt. of $Ag_4P_2O_7$	White gelatenous ppt. $AgPO_3$
2. Neutral barium chloride solution.	White ppt. soluble in acetic acid.	White ppt. insoluble in acetic acid.	White ppt. insoluble in acetic acid.
3. Magnesia mixture.	White ppt.	White ppt. which is soluble in excess of the reagent.	No ppt.
4. Cobalt nitrate solution.	Bluish white ppt.	Pink ppt.	No ppt.

• Metaphosphorus acid HPO_2 is not known—Explain.

While metaphosphoric acid is known, metaphosphorus acid HPO_2 is not known. This is because meta acids are obtained by heating corresponding ortho acids by loss of one molecule of water.



Similarly Meta phosphorous acid is expected to form from ortho phosphorous acid by loss of water but the resulting compound does not contain any OH group and cannot be regarded as acid.



5.15. Justification of placing nitrogen and phosphorus in the same group in the periodic table.

Nitrogen differs from phosphorus in many respects. (i) Nitrogen is an inert, non combustible gas, while phosphorus is most active and highly inflamable solid. (ii) Nitrogen occurs in free state but phosphorus does not. (iii) Nitrogen molecule is diatomic (N_2) while phosphorus is tetratomic (P_4). (iv) Nitrogen exhibits a number of oxidation states such as (−3) in NH_3, (−2) in (N_2H_4), (−1) in (NH_2OH), (+1) in (N_2O), (+2) in (NO) (+3) in (N_2O_3), (+4) in (NO_2) and (+5) in (N_2O_5) but phosphorus does not exhibit such a variety of oxidation states. (v) The hydride of nitrogen is stable and non-poisonous while that of phosphorus is less stable and highly poisonous. (vi) Nitrogen does not directly react with halogens, sulphur, alkalis or nitric acid but phosphorus directly reacts with these substances.

Inspite of all these differences, the two elements have been placed in the same group (VB) in the periodic table due to the following reasons.

1. Electronic configuration : The atomic number of nitrogen is 7 and its electronic configuration is $1s^2\ 2s^2\ 2p^3$. The atomic number of phosphorus is 15 and its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$. Both the elements have five valence electrons in their outermost orbit.

2. Both nitrogen and phosphorus are exclusively *non-metals.*

3. Both the elements are *polyvalent.* Ordinarily both of them form compounds in tri and penta valent states, e.g., NH_3, N_2O_5, PH_3, P_2O_5. In addition to these, other valencies are also exhibited by these two elements.

4. Oxidation states : The maximum oxidation state exhibited by N_2 is $+5$, besides this the other oxidation states exhibited by it are $-3, -2, -1, +1, +2, +3, +4$. The maximum oxidation state exhibited by phosphorus is $+5$ and the others are $-3, -2, +1$, and $+3$.

5. Allotropy : Both N_2 and P_4 exhibit allotropy.

6. Hydrides : Both the elements form similar type of hydrides. N_2 forms 3 hydrides, e.g., NH_3,N_2H_4 and N_3H, while P forms only two e.g., PH_3 and P_2H_4. Ammonia is stable, basic in nature and very soluble in water. On the otherhand phosphine is unstable, feebly basic and sparingly soluble in water.

7. Oxides : Both the elements form a number of oxides. N_2 combines directly with O_2 at 3000°C forming NO, while P combines directly with O_2 at ordinary temperature, with the formation of P_2O_3 and P_2O_5. Only two oxides (N_2O, NO) of nitrogen are neutral and others are acidic, but all the oxides of phosphorus are acidic in nature.

8. Oxyacids : Both of them have more than one oxyacids. The chief oxyacids of N_2 are HNO_3 and HNO_2. The chief oxyacids of phosphorus are H_3PO_4 and H_3PO_3. The oxyacids of N_2 are stronger than those of P.

9. Chlorides : N_2 combines with Cl_2 producing NCl_3 which is very unstable. It undergoes hydrolysis. P combines with Cl_2 forming PCl_3 and PCl_5 which are stable and undergo hydrolysis. N_2 has no pentachloride.

10. At high temperature both N_2 and P_4 directly combine with metals like Ca, Mg, Al with the formation of their nitrides and phosphides respectively. These compounds react with water to liberate NH_3 and PH_3 respectively.

$$\begin{aligned} 3Ca + N_2 &= Ca_3N_2 \qquad & Ca_3N_2 + 6H_2O &= 3Ca(OH)_2 + 2NH_3 \\ 3Ca + 2P &= Ca_3P_2 \qquad & Ca_3P_2 + 6H_2O &= 3Ca(OH)_2 + 2PH_3 \end{aligned}$$

- **Nitrogen forms NCl_3 but phosphorus can form PCl_3 and PCl_5—explain.**

Nitrogen belongs to second period in the peridic table and its electronic arrangement is $1s^2\ 2s^2\ 2p^3$.Consequently N-atom uses its 3 electrons of *p* orbital to form three N−Cl bonds having a lone pair. Thus NCl_3 is formed. N atom can not exceed the limit of octet as it has no *'d'* orbital. On the other hand the electronic structure of P atom is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$. Thus the 3d orbital in N atom lies vacant. So even after forming 3 P−Cl bonds, it can utilise its *3d* orbital and expand its co-ordination number beyond three. Hence it can form both PCl_3 and PCl_5.

- **Fertilizer—super phosphate of lime :**

The chemical which is added to soils to make up the defficiency of elements for the growth of plants are known as fertilizers. A compound which is to be used as fertilizer must have the following properties :—

(i) The elements present in the fertilizer should be easily assimilated by the plants. (ii) It must be soluble in water. (iii) It must be very stable so that the plants can use it for a long time. (iv) There should not be any major change in the *pH* of the soil by its application. (v) It should not be injurious to plants. (vi) It should be cheap.

Thus phosphorus is one of such elements which stimulates the growth of plants. The phosphate fertilizers are—*super phosphate of lime, double* and *triple super phosphate.*

Preparation of super phosphate of lime :

Finely powdered phosphate rock or bone ash is treated with two third of its weight of 60–70% H_2SO_4 in a cast iron mixer fitted with revolving blades. The contents are mixed together intimately for 2 minutes and then dumped in a closed vessel for 24 hours. Here different reactions take place and as a result the temperature rises with the evolution of gases like CO_2, HCl, SiF_4 etc., which escape through an outlet. The product which is a mixture of *mono calcium phosphate* [$Ca(H_2PO_4)_2$] and *calcium sulphate is collectively known as super phosphate of lime.*

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = Ca(H_2PO_4)_2 + 2(CaSO_4, 2H_2O)$$

It contains about 16% available phosphorus. The mono calcium phosphate is soluble in water and hence readily assimilated by plants.

• Some solved problems :

1. *A white solid (A) on being reacted with 60% H_2SO_4 yields an insoluble solid (B) and a liquid (C). When (C) is heated, an acid (D) is obtained. A mixture of the acid (D) with charcoal powder is dried and the dried residue is heated strongly in a retort and the distillates are passed through water, when a white residue (E) is found to condense in water. This white solid when brought in contact with air burns and white fumes (F) are produced. Identify A, B, C, D, E and F.*

Ans : (A) is calcium phosphate, (B) is calcium sulphate, (C) is phosphoric acid, (D) is meta phosphoric acid, (E) is white phosphorus and (F) is phosphorus pentoxide.

The reaction involved are—

(i) $\underset{[A]}{Ca_3(PO_4)_2} + 3H_2SO_4 = \underset{[B]}{3CaSO_4\downarrow} + \underset{[C]}{2H_3PO_4}$

(ii) $\underset{[C]}{H_3PO_4} \xrightarrow[\Delta]{} \underset{[D]}{HPO_3} + H_2O\uparrow$

(iii) $\underset{[D]}{4HPO_3} + 12C = 12CO\uparrow + 2H_2\uparrow + \underset{[E]}{P_4\uparrow}$

(iv) $\underset{[E]}{P_4} + 5O_2 = \underset{[F]}{P_4O_{10}}$

2. *A white solid (A) on being heated to 250°C* is an atmosphere of inert gas in presence of I_2 yields a red solid (B). When (B) is treated with conc. HNO_3 a tribasic acid (C) is obtained. When (A) is heated with conc. NaOH solution in an atmosphere of coal gas yields a gas mixture which when passed through a U-tube kept in freezing mixture, liquid (D) is obtained and the other gas (E) passes out. (D) when comes in contact with air burns spontaneously. When (E) is passed through $CuSO_4$ solution, a ppt (F) is obtained. Identify A, B, C, D, E and F and give the equation of the reactions which take place.

Ans. (A) is white P, (B) is red P, (C) is ortho phosphoric acid (H_3PO_4) (D) is phosphorus dihydride (P_2H_4), (E) is phosphine (PH_3), (F) is copper phosphide (Cu_3P_2).

The reactions which take place—

(i) $\underset{[A]}{\text{White}} \xrightarrow[I_2\,\text{Cat}]{250^\circ C} \underset{[B]}{\text{Red P}}$

(ii) $\underset{[B]}{4P} + 10HNO_3 + H_2O = \underset{[C]}{4H_3PO_4} + 5NO + 5NO_2$

(iii) $\underset{[A]}{P_4} + 3NaOH + 3H_2O = \underset{[E]}{PH_3} + 3NaH_2PO_2$

(iv) $\underset{[A]}{6P} + 4NaOH + 4H_2O = \underset{[D]}{P_2H_4} + 4NaH_2PO_2$

(v) $3CuSO_4 + \underset{[E]}{2PH_3} = \underset{[F]}{Cu_3P_2} + 3H_2SO_4$

• Exercises •

1. (a) How does phosphorus occur in nature ? Why is it not found in free state in nature ? [*W.B.H.S.* '79]

(b) Name the principal allotropes of phosphorus.

(c) What is bone ash ? Describe the preparation of white phosphorus from bone ash. [*W.B.H.S.* '83]

2. How white phosphorus can be prepared from phosphoric acid and vice versa ? [*W.B.J.E.* '83]

3. What are the sources of phosphorus in nature ? Describe the electrothermal process of the preparation of white phosphorus from mineral phosphates. [*W.B.H.S.* '89, '90, (T) '82]

4. (a) Mention the chief uses of white phosphorus ? How is it stored ? [*W.B.J.E.* '92]

(b) What is allotropy ? Name the two allotropes of phosphorus.

5. (a) State briely giving all conditions, the process by which white phosphorus can be transformed into red phosphorus. Write down the name of the catalyst used in it.

[*W.B.H.S.* '82, '93, *W.B.J.E.* '82, '90]

6. Compare the properties of white phosphorus with those of red phosphorus. What is phosphorescence of phosphorus ? [*H.S.(T)* '83]

7. Starting from mineral phosphates or bone ash how would you prepare —(i) White phosphorus, (ii) Red phosphorus, (iii) Phosphorus pentoxide, (iv) Ortho phosphoric acid, (v) Phosphorus trichloride.

8. (a) How is phosphine prepared in the laboratory ? Give a neat diagram of the apparatus used. How is the gas collected ? [*W.B.H.S.* '82, *W.B.J.E.* '90]

(b) Compare the properties of phosphine with those of ammonia. [*H.S.(T)* '89, *W.B.J.E.* '82]

(c) Mention a reaction to prove the basic nature of phosphine. [*W.B.H.S.* '83]

(d) Which one is more basic ammonia or phosphine ? Give reasons. [*W.B.J.E.* '90]

(e) What happen when PH_3 is passed into an acidified solution of $CuSO_4$. [***W.B.H.S.*** **'96**]

9. (a) How would you prove the reducing property of phosphine ?

(b) Mention two reactions to show that white phosphorus is more active than red phosphorus.

[*W.B.H.S.* '80, '90]

10. Justify the placing of nitrogen and phosphorus in the same group of the periodic table.

11. How would you prepare phosphorus trioxide and phosphorus pentoxide from white phosphorus ? Discuss the action of water on these two oxides. Prove that P_2O_5 is a dehydrating agent.

12. (a) How is phosphorus acid prepared in the laboratory ? Give two reactions showing its reducing property. What is the anhydride of H_3PO_3 ? [*W.B.J.E.* '89]

(b) Comment on the basicity of phosphorus acid. [*W.B.J.E.* '83]

13. (a) How can orthophosphoric acid be obtained from bone ash or phosphatic minerals ?

[*W.B.H.S.* '90, *W.B.J.E.* '83]

(b) Discuss the action of heat on ortho phosphoric acid. [*W.B.H.S.* '86, *W.B.J.E.* '83] or, Give the necessary chemical equations showing the relation between P_2O_5, HPO_3 and H_3PO_4 [*H.S.* '92]

(c) Discuss the properties of phosphoric acid. [*W.B.J.E.* '83]

14. Give the structural formula of phosphorus acid and orthophosphoric acid. Compare the properties of H_3PO_3 with those of H_3PO_4. [*Tri. H.S.* '83]

15. (a) Give the necessary chemical principle with equation for the preparation of phosphoric acid from phosphorus. [*W.B.J.E.* '83]

(b) What is super phosphate of lime ? Describe its uses. [*H.S.* '90, '92]

16. Prove that :—

(i) Ortho phosphoric acid contains phosphorus.

(ii) Phosphine contains phosphorus. [*H.S.* '83]

(iii) Calcium phosphate contains phosphorus.

(iv) Phosphorus trioxide and P_2O_5 contain phosphorus.

(v) Phosphorus acid contains phosphorus.

(vi) White and red phosphorus are essentially the same element.

(vii) PH_3 is a reducing agent.

(viii) P_2O_5 is a strong dehydrating agent.

(xi) PH_3 is alkaline.

(xii) P_2O_3 is an acidic oxide.

17. How would you remove :—

(i) White phosphorus from red phosphorus. [*W.B.J.E.* '85]

(ii) P_2O_3 from P_2O_5, (iii) Phosphorus dihydride from phosphine, (iv) Ammonia from phosphine, (v) PCl_5 from PCl_3, (vi) P_2O_5 from phosphorus.

18. Giving equations describe how would you distinguish between :

(a) Red phosphorus and white phosphorus. [*Jt. Ent.* '91]

(b) Phosphorus acid and phosphoric acid.

(c) Ammonia and phosphine. [*Jt. Ent.* '92]

(d) Phosphorus trioxide and phosphorus pentoxide.

(e) Nitric acid and phosphoric acid.

(f) Phosphorus dihydride and phosphine.

19. How could you obtain :

(a) Phosphoric acid from bone ash.

(b) Phosphine from phosphonium salt.
(c) Phosphine from phosphorus acid and vice versa.
(d) White P and red P from phosphoric acid. [*Jt. Ent.* '83]
(e) Phosphorus acid from phosphoric acid and vice versa.
(f) Orthophosphoric acid from P_2O_5. [*H.S.* '79]
(g) Phosphoric acid from phosphorus. [*H.S.* '79]
(h) Phosphine from CaO and white P. [*W.B.H.S.* '96]
(i) H_3PO_4 from $Ca_3(PO_4)_2$.
(j) Pyro phosphoric acid and phosphorus acid from $Ca_3(PO_4)_2$

20. Explain why :—
(a) Nitrogen is a gas at ordinary temperature but phosphorus is a solid. (b) White phosphorus is kept in water. (c) The m.p. and b.p. of ammonia are higher than those of phosphine. (d) Phosphorus acid behaves as dibasic acid though three H-atoms are present in its molecule. [*W.B.J.E.* '90] (e) Ammonia is more basic than phosphine. [*W.B.H.S.* '91] (f) At high temperature (1150°C) silica replaces the more acidic oxide P_2O_5 from $Ca_3(PO_4)_2$. [*W.B.J.E.* '88] (g) During the laboratory method of preparation of phosphine, the air inside the flask is replaced by coal gas [*W.B.H.S.* '87, '88] (h) Phosphine prepared by the action of NaOH solution on white P catches fire in contact with air, though it is not spontaneously inflamable in air. (i) Na_2H, PO_3 is a normal salt [*T.H.S.*. '84] (j) White phosphorus is more reactive than red phosphorus [*W.B.J.E.* '92, *W.B.H.S.* '80]. (k) PH_3 is more stronger reducing agent than NH_3. (l) Phosphorus does not occur in free state in nature. [*W.B.H.S.* '79] (m) If one touches white P, one's hands are to be washed with $CuSO_4$ solution [*W.B.H.S.* '86]. (n) Phosphorus acid has reducing property. (o) The molecular formula of phosphorus acid should not be $P(OH)_3$. (p) Ortho phosphoric acid behaves as a dibasic acid. [*W.B.H.S.* '91] (q) PCl_3 though a covalent compound, its aqueous solution conducts electricity. [*H.S.* '92] (r) Na_2PO_3 salt does not exist. (s) Red P is less volatile than white P. [*I.I.T.* '82] (t) Phosphoric acid is tribasic but phosphorus acid is dibasic. [*I.I.T.* '87, '89] (u) Nitrogen can only form NCl_3 but phosphorus can form both PCl_3 and PCl_5. (v) White P and red P are the allotropes of the same element. (w) NH_3 has a higher boiling point than pH_3 [*I.I.T. '89*], (x) Red P is denser than white P. (y) Ortho phosphoirc acid is a syrup liquid. (z) PCl_5 exists but NCl_5 does not.

21. Describe with equations what happens when— (a) A mixture of bone ash, silica and coke is heated at high temperature. [*H.S.* '78] (b) Red phosphorus is heated with conc. HNO_3 and the liquid obtained is heated gradually. [*T.H.S.* '91] (c) Oxygen and chlorine are reacted with phosphorus separately. [*W.B.H.S.* '87] (d) White P is boiled with caustic soda or caustic potash. [*W.B.H.S.* '88, '91, '93, *T.H.S.* '86 *I.I.T.* '87] (e) A mixture of conc. HNO_3 and P_2O_5 is heated. (f) Phosphine is passed through acidified solutions of copper sulphate. [*W.B.H.S.* '80, '92, *T.H.S.* '87] (g) White P is heated at 250°C in a closed vessel in an inert atmosphere. (h) White P is treated with $AgNO_3$ solution. [*W.B.J.E.* '88] (i) A mixture of P_2O_5 and powdered coke is heated at 1500°C. (j) White P is added to copper sulphate solution. (k) Bromine is added dropwise to a mixture of red phosphorus and water. [*W.B.H.S.* '87]° (l) Phosphoric acid is gradually heated to high temperature. [*W.B.J.E.* '86]. (m) White P is brought in contact with iodine. (n) Calcium phosphate is heated with strong H_2SO_4. (o) A paste of BaO_2 is added to dil. H_3PO_4. (p) Phosphorus pentoxide is boiled with water. (q) Phosphorus acid is heated strongly. (r) H_3PO_3 is treated with acidified solution of potassium permanganate. (s) Phosphorus tri chloride is treated with water. (t) Water is added gradually to a mixture of red phosphorus and iodine. [*H.S.* '91] (u) Phosphine is passed through an aqueous solution of bleaching powder. [*Jt. Ent.* '92] (v) Calcium phosphate is added to a mixture of silica and coke and the mixture is heated strongly. [*I.I.T.* '85] (w) Hypophosphorus acid is heated. [*I.I.T.* '89] (x) White phosphorus is added to $AgNO_3$ solution. (y) White phosphorus is added to a solution of baryta [$(Ba(OH)_2$]. (z) White phosphorus is treated with concentrated H_2SO_4.

22. Compare the properties of P_2O_3 with those of N_2O_3. [*Tri. H.S.* '83]

23. A liquid may be a solution of H_3PO_3 or H_3PO_4. Mention two chemical tests by which they can be identified.

24. (A) is a white solid which melts at 44°C. When (A) is boiled with conc. NaOH a gas (B) is obtained which inflames when comes in contact with air. (A) when heated to 250°C in a closed vessel in an inert atmosphere, a red coloured substance (C) is obtained. (C) on being heated to 560°C in an inert atmosphere yields (A). Identify (A), (B) and (C). [***Ans.*** A = white P, B = PH_3, C = red P]

25. A white solid (A) when brought in contact with air catches fire and a dense white smoke of (B) is produced. (B) on being treated with hot water yields (C) which turns blue litmus red. Identify (A), (B) and (C).
[***Ans.*** A = white P, B = P_2O_5, C = H_3PO_4]

26. A white solid (A) reacts with calcium forming (B). (B) on treatment with water produces a gas (C). (A) when treated with caustic potash solution yields (C). (C) on being treated with HCl produces (D). Identify (A), (B), (C) and (D). [***Ans.*** A = white P, B = Ca_3P_2, C = PH_3, D = PH_4Cl.]

27. (a) How is phosphoric acid detected and distinguished from phosphorus acid ?

(b) How would you convert H_3PO_4 into H_3PO_3 and vice-versa ?

(c) P_2O_3 is an anhydride of phosphorus acid. Will it produce H_3PO_4 with water ? If so, under what condition ?

(d) What are the functions of coke and silica in the preparation of white P from phosphatic minerals ?

(e) How would you obtain phosphorus from magnesium phosphate and phosphine ?

(f) Give the structural formula of phosphorus acid and pyro phosphoric acid. [*I.I.T.* '81]

28. A solution containing 3 moles of KOH is added to a solution containing 2 moles of H_3PO_4. Water is evaporated. What is the composition of the crystals precipitated ? [*W.B.J.E.E.* '91]

[*Ans.* $2H_3PO_4 + 3KOH = K_2HPO_4 + KH_2PO_4 + 3H_2O$]

• Objective type questions.

(A) *Thought type :*

(a) Which of the following is a metalloid ?—(i) P, (ii) N, (iii) As, (iv) Bi [**Ans** : As]

(b) Which of the following is most acidic ? (i) P_2O_3, (ii) Bi_2O_3, (iii) As_2O_3 [**Ans** : (i)]

(c) Which of the oxides is amphoteric ? (i) N_2O_5, (ii) P_2O_3, (iii) Al_2O_3, (iv) As_2O_3 [**Ans** : (iii)]

(d) It is difficult to pull electrons from N-atom because—

(i) N_2 is a gas, (ii) valence shell is closer to neucleus, (iii) it has small number of electrons. [**Ans** : (ii)]

(e) Ignition point of white P is (i) 35°C, (ii) 250°C, (iii) 100°C. [**Ans** : (i)]

(f) Red P is chemically less active than white P because—

(i) it has polymeric structure, (ii) it is red in colour, (iii) it does not contain P – P bond, (iv) it does not contain tetrahedral molecules. [**Ans** : (i)]

(g) The two H-atoms in H_3PO_3 are acidic because—

(i) all the H-atoms are attached to P atom, (ii) two H-atoms are attached to O-atoms, (iii) all the H-atoms are attached to O-atoms. [**Ans** : (ii)]

(B) *Complete the following equations :*

(a) $P_4 + \text{—} + H_2O \rightarrow PH_3 + NaH_2PO_2$

(b) $H_3PO_3 \rightarrow H_3PO_4 + \text{—}$

(c) $P_4 + CuSO_4 + H_2O \rightarrow Cu + \text{—} + H_2SO_4$

(d) $P_4 + \text{—} + H_2O \rightarrow H_3PO_4 + NO + NO_2$

(e) $P + NaOH + H_2O \rightarrow P_2H_4 + NaH_2PO_2$

(f) $AgNO_3 + PH_3 \rightarrow Ag_3P$; $3AgNO_3 + HNO_3$

(g) $CuSO_4 + H_3PO_3 + - \rightarrow Cu + - + H_2SO_4$

(C) *Pick up the correct one(s) :*

(a) The molecular formula of phosphorus is (i) P, (ii) P_2, (iii) P_3, (iv) P_4 [**Ans** : (iv)]

(b) The increasing order of basicity of hydride of Gr V element is (i) NH_3, PH_3 SbH_3, AsH_3, (ii) PH_3, NH_3, AsH_3 SbH_3, (iii) SbH_3, AsH_3 PH_3 NH_3 [**Ans** : (iv)]

(c) In P_4O_6 and P_4O_{10}, P undergoes hybridisation— (i) *sp*, (ii) sp^2, (iii) sp^3, (iv) dsp^2 [**Ans** : (iii)]

(d) The high reactive and low volatility of white phosphorus is because of— (i) it contains tetrahedrally arranged P_4 units, (ii) stearic strain is high, (iii) high electronegativity of P atom. [**Ans** : (i)]

(e) A person working with P suffers from (i) scurvy, (ii) rickets, (iii) phossy jaw. [**Ans** : (iii)]

(f) PCl_3 on hydrolysis yields— (i) HPO_3, (ii) H_3PO_4, (iii) H_3PO_2, (iv) H_3PO_3 [**Ans** : (iv)]

(g) Non combustible hydride is (i) NH_3, (ii) PH_3, (iii) AsH_3. [**Ans** : (i)]

(h) P forms five bonds due to sp^3d hybridisation, N does not form penta halides which is due to— (i) small size of N-atom, (ii) less atomic number of N, (iii) absence of *d* orbital, (iv) high electronegativity of N. [**Ans** : (iii)]

(i) Phosphorus acid is— (i) a tribasic (ii) dibasic, (iii) menobasic. [**Ans** : (ii)]

(j) For softening hard water salt of oxyacid of P used is— (i) calgon, (ii) micro cosmic salt, (iii) chlorapatite. [**Ans** : (i)]

(k) $AgNO_3$ reacts with PH_3 to give (i) silver phosphate, (ii) silver phosphite, (iii) silver phosphide, (iv) silver. [**Ans** : (iii)]

(l) Ammonia and phosphine resemble each other in (i) solubility, (ii) basic character, (iii) stability, (iv) reducing property. [**Ans** : (ii)]

(m) P on heating with conc. HNO_3 gives— (i) P_4O_6, (ii) P_4O_{10}, (iii) H_3PO_3, (iv) H_3PO_4 [**Ans** : (iv)]

(n) Which of the following is strongest reducing agent— (i) PH_3, (ii) NH_3, (iii) AsH_3. [**Ans** : (iii)]

(o) Conc. HNO_3 on being heated with P_2O_5 yields (i) N_2O, (ii) NO, (iii) N_2O_3, (iv) NO_2, (v) N_2O_5. [**Ans** : (v)]

(p) White P reacts with caustic soda with the formation of PH_3 and NaH_2PO_2. The reduction is an example of (i) oxidation, (ii) reduction, (iii) disproportionation, (iv) neutralisation. [**Ans** : (iii)] [*I.I.T.* '80]

6

SULPHUR AND ITS COMPOUNDS

• Sulphur •

Symbol—S. **Atomic No.—16** **Atomic weight 32·06**
Electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^3\ 3p^4$ **Oxidation number : (−2), (+1), (+4), (+6)**

The uses of sulphur specially in medicines were known from the ancient times. Its reference is found in the Bible as '*brim stone*'. Lavoisier in 1774 studied its properties and recognised it as an element.

6.1. Natural sources of sulphur.

Sulphur is widely distributed in nature both in the free state as well as in combination with other elements. In combined state sulphur occurs as *sulphides* and *sulphates* of many metals, eg.

(i) *Iron pyrites* (FeS_2), (ii) *Copper pyrites* (Cu_2S, Fe_2S_3), (ii) *Galena* (PbS), (iv) *Zinc blend* (ZnS), (v) *Gypsum* ($CaSO_4$, $2H_2O$), (vi) *Barytes* ($BaSO_4$), (vii) *Kiesserite* ($MgSO_4$, H_2O).

6.2. Extracion of Sulphur.

Deposits of free sulphur are found to occur in abundance in nature, particularly in the volcanic regions. Two methods are generally employed for the extraction of sulphur from its deposits—

(i) *Sicilian process,* (ii) *American or Frasch process.*

(1) **Sicilian process :** (a) This process is mainly used for working up the *Italian deposits*. Sulphur bearing rocks which are found in Italy, contains (20—25)% free sulphur along with other impurities, such as clay, sand, limestone, etc.

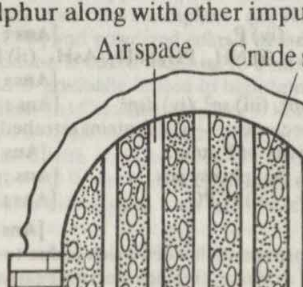


Fig. 6.1 : Sicilian process

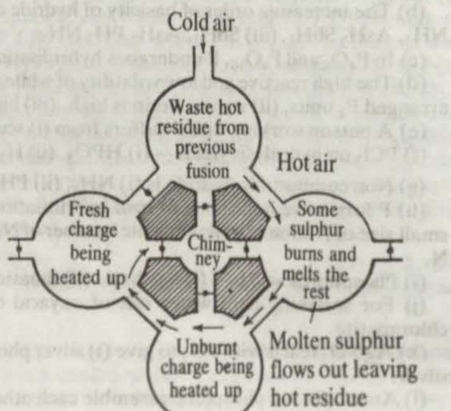

Cold air
Waste hot residue from previous fusion
Hot air
Fresh charge being heated up
Chim-ney
Some sulphur burns and melts the rest
Unburnt charge being heated up
Molten sulphur flows out leaving hot residue

Fig. 6.2 : Regenarative Kiln

In this process the sulphur rocks are stacked on the sloping floor of a brick-made kiln. Crude sulphur is heaped on the floor in such a way as to leave air spaces in

between. The sulphur rocks are ignited at the top. About one-third of the sulphur is burnt and escapes as SO_2. This reaction is highly exothermic and the heat generated from the reaction melts the remaining portion of sulphur which flows down the sloping floor into a wooden trough. The sulphur thus obtained, contains about 5% rockly impurities. This method is sufficiently wasteful as about 33% of sulphur is lost during the burning.

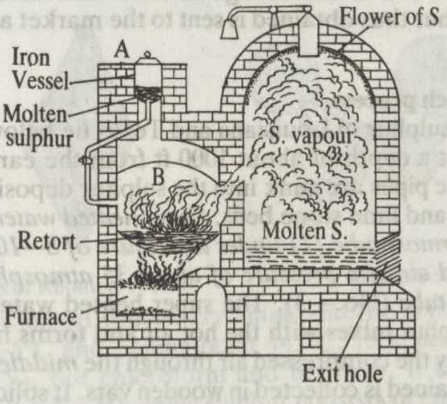


Fig. 6.3 : Refining of crude sulphur

(b) An improved kiln in which wastage of sulphur is avoided, is known as *Gills regenarative kiln*. It consists of four brick chambers arranged in a circle. Each chamber is connected with the other and with a chimney built at the centre. Some of

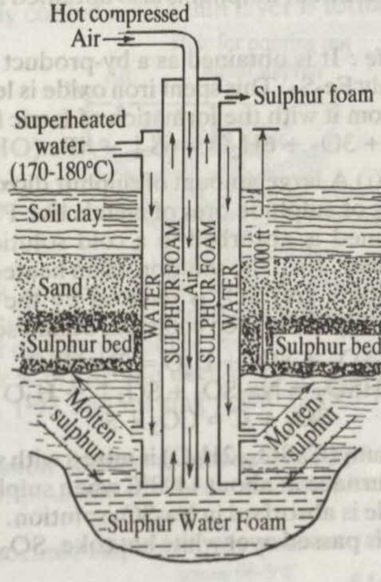


Fig. 6.4 : Frasch process of extracting of sulphur

the sulphur is made to burn in one of the chambers and the hot gases generated are allowed to pass to the other chambers where the sulphur melts and flows down into the wooden vats. Thus the process continues in series and as a result the fuel expense is minimised.

(c) *Purification* : The impure sulphur thus obtained, is at first heated in an iron vessel from which the molten sulphur flows down into a cast iron retort heated by fire. Sulphur boils and the vapours generated are led into a large chamber made of bricks where the sulphur vapours condense on the cold walls as light yellow powder called *flowers of sulphur*. Later on, as the walls of the chamber are heated up above 120°C, the sulphur melts. The pure molten sulphur collects on the floor of the chamber from where it is drawn out through an outlet and cast into sticks in wooden moulds. The pure sulphur thus obtained is sent to the market as *roll of sulphur*.

(2) **American or Frasch process.**

The deposits of free sulphur in Louisiana and Texas lie below the layers of clay, sand and lime stones at a depth of about 1000 ft from the earth's surface. In this process three concentric pipes are sunk into the sulphur deposit by boring through the layers of clay, sand and lime stone beds. *Super heated water* (170°C) is pumped down through the *outermost tube (1) under a pressure of 8—10 atmospheres* and a blast of *hot compressed air at a pressure of about 35 atmospheres* is then passed through the *innermost tube* (No.—3). The super heated water melts the sulphur below. This molten sulphur mixes with the hot air and forms froth of low density. This froth is forced up by the compressed air through the *middle pipe* (No.—2). The molten sulphur thus obtained is collected in wooden vats. It solidifies on cooling and is separated from water. Sulphur obtained by this precess is about 99·5% pure.

(3) **Extraction of sulphur from other sources.**

In countries where sulphur does not occur in free state, it is extracted from some other sources. One of such sources is the *spent iron oxide* which is obtained as a by-product in the coal gas preparation. Sulphur is also obtained from different sulphide and sulphate ores.

(a) *From spent iron oxide :* It is obtained as a by-product in the manufacture of coal gas. It consists of mainly Fe_2S_3. This spent iron oxide is left exposed to air when free sulphur is separated from it with the formation of ferric hydroxide.

$$2Fe_2S_3 + 3O_2 + 6H_2O = 6S\downarrow + 4Fe(OH)_3$$

(b) *From sulphide ores :* (i) A large amount of sulphur dioxide is obtained as a by-product during the roasting of sulphide ores of metals like Pb, Cu, Zn etc. (ii) The sulphur dioxide thus obtained is absorbed in a cold solution of *sodium sulphite* containing *aluminium sulphate.* (iii) The solution when heated SO_2 is evolved which is passed over white hot coke. (iv) SO_2 is reduced by the coke to produce free sulphur. (v) The vapour of sulphur is then cooled to obtain solid sulphur.

$$Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3$$
$$2NaHSO_3 = Na_2SO_3 + SO_2\uparrow + H_2O$$
$$SO_2 + C = CO_2 + S$$

(c) *From gypsum :* Gypsum ($CaSO_4, 2H_2O$) is mixed with sand, clay and coke and the mixture is heated in a furnace at about 1400°C when sulphur dioxide is evolved. The evolved sulphur dioxide is absorbed in Na_2SO_3 solution. This solution on being heated, evolves SO_2 which is passed over white hot coke. SO_2 is reduced by the coke to produce free sulphur.

6.3. Allotropic modification of sulphur.

Like carbon and phosphorus, sulphur also exhibits allotropy. It exists in a number of allotropic forms which possess different physical characteristics.

[A] Crystalline allotropes :

(i) Rhombic or Octahedral or α sulphur.

When roll sulphur is dissolved in carbon di-sulphide and the solution is slowly evaporated, transparent lemon yellow octahedral cryatals of rhombic sulphur are obtained. At an ordinary temperature this is the most stable form of sulphur. All other allotropic forms of sulphur are gradually converted to this form.

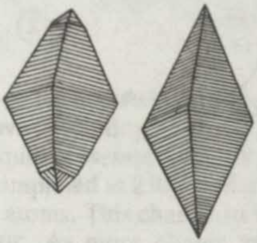


Fig. 6.5 : Crystals of Rhombic sulphur

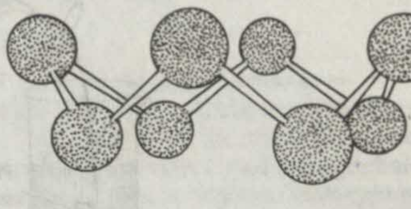


Fig. 6.6 : Sulphur molecule

Rhomic sulphur is lemon yellow, crytalline and the crystals are octahedral. Its melting point is 114·5°C and boiling point 445°C. Its specific gravity is 2·06. It is readily soluble in CS_2, hot chloroform and benzene. It cannot conduct heat or electricity. Its formula is S_8. Rhombic sulphur consists of eight numbered puckered rings of sulphur atoms connected to one another by single covalent bond.

(ii) Monoclinic or prismatic or β sulphur.

At about 96·5°C, the rhombic form of sulphur is converted to monoclinic form. This form of sulphur is obtained by melting rhombic sulphur in a porcelain dish. The molten sulphur is slowly cooled until a thin layer is formed at the surface. A hole is made in the crust thus formed and the molten sulphur inside is poured off. On removing the crust, needle shaped, transparent yellow crytals of monoclinic sulphur are found to be formed on the wall of the dish.

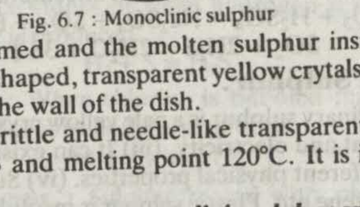


Fig. 6.7 : Monoclinic sulphur

This form of sulphur is brittle and needle-like transparent crystals. The specific gravity of this form is 1·93 and melting point 120°C. It is insoluble in water but soluble in CS_2.

- ***Conversion of rhombic sulphur to monoclinic sulphur and vice-versa.***

The rhombic sulphur pass into the monoclinic sulphur when the rhombic form is heated above 96·5°C.

The crystals of monoclinic sulphur slowly pass into rhombic sulphur when kept below 96·5°C.

$$\underset{\text{Rhombic form}}{S(\alpha)} \xrightleftharpoons[\text{below } 96{\cdot}5^\circ C]{\text{above } 96{\cdot}5^\circ C} \underset{\text{Monoclinic form}}{S(\beta)}$$

Thus monoclinic form may be converted into the rhombic form and vice-verse.

[B] Amorphous sulphur :

(i) **Plastic sulphur.**

The amorphous form of sulphur is obtained by heating the roll of sulphur nearly to its boiling point, when it is converted to a dark brown liquid. This dark brown liquid is then poured in a thin stream into cold water in a beaker. It solidifies into a dark brown rubber like mass. This is known as *plastic sulphur.*

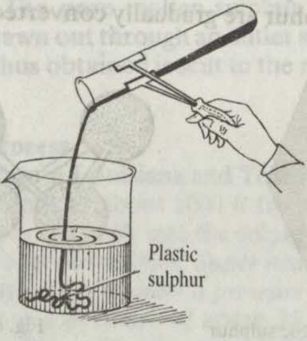


Fig. 6.8 : Plastic sulphur

Plastic sulphur is a brown coloured elastic solid. Its specific gravity is 1·95. Plastic sulphur is insoluble in water *as well as in carbon di-sulphide.* It is unstable and at ordinary temperature it is converted to rhombic sulphur.

(ii) **Milk of sulphur.**

This form of sulphur is obtained by boiling flowers of sulphur with water and milk of lime, when a red coloured solution of calcium pentasulphide is obtained. The solution is filtered and treated with hydrochloric acid when a white amorphous variety precipitates out which is called milk of sulphur.

$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S \downarrow$$

Its speceific gravity is 1·82. It is insoluble in water but soluble in CS_2. This variety tends to revert to the rhombic variety if kept over a long period.

(iii) **Colloidal sulphur :** (a) This variety of sulphur is obtained as a milky suspension by passing H_2S through a saturated solution of *sulphur di-oxide* or (b) by adding conc. H_2SO_4 to a saturated solution of *sodium thiosulphate.*

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O + S \downarrow$$
$$SO_2 + 2H_2S = 2H_2O + 3S \downarrow$$

6.4. Properties of Sulphur.

[A] ***Physical :*** (i) Ordinary sulphur is a pale yellow crystalline solid. (ii) It is brittle and cannot conduct heat and electricity. (iii) It can exist in a number of allotropic forms which possess different physical properties. (iv) Sulphur is insoluble in water but soluble in CS_2, benzene etc. Plastic sulphur is insoluble in CS_2.

- **Action of heat on sulphur :**

Sulphur exhibits remarkable changes when it is heated gradually. (i) Rhombic sulphur melts at 110°C—119°C to a *clear mobile* and *pale yellow liquid.* (ii) On further heating instead of becoming more mobile it becomes *thicker* and *darker* and turns to a *deep orange liquid.* (iii) At 160°C—180°C it becomes *almost immobile* and *viscous.* (iv) At 230°C its colour becomes *black* and its *viscosity increases.* (v) Beyond 230°C it becomes *mobile* again. (vi) At 444·6°C it begins to boil giving off *yellow vapours.* (vii) When the boiling sulphur is allowed to cool down slowly reverse changes occur.

Explanation : This abnormal behaviour of sulphur is due to the fact that the molecules of sulphur are composed of 8 atoms arranged in a closed puckered ring.

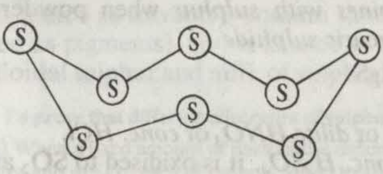


Fig. 6.9 : Puckered ring

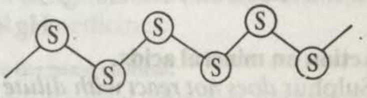


Fig. 6.10 : Chain structure

Just above its melting point such type of molecules can easily slip over the other and so the liquid possesses mobility. At above 160°C rapture of the ring structure begins and is completed at 230°C when the ring structures are converted to large chains of sulphur atoms. This change in the molecular structure is exhibited in deepening of its colour. As more chains are formed they become tangled and lengthen by interlinking and thus large chains of sulphur atoms are formed. As a result the viscosity of the liquid increases, and the liquid loses its mobility. When the temperature is further increased, the larger chains break up into smaller fragments and as a result the mobility of the liquid increases again. The liquid becomes darker in colour, till at 444·6°C it takes the form of a black liquid and begins to boil giving off a yellow vapour.

At still higher temperatures the vapour of S_8 molecules dissociates forming S_6, S_4 and S_2 molecules. At 1000°C the vapour density corresponds to the formula S_2 and at 2000°C monatomic molecules of sulphur are produced.

[B] ***Chemical*** **:** Sulphur is inert at ordinary temperature but when it is heated, it becomes very active and reacts with a larger number of elements.

1. **Action on non-metals :**

(i) *Action on air or O_2 :* When sulphur is strongly heated in air or oxygen, it combines with oxygen to form *sulphur dioxide,* with a trace of *sulphur trioxide.*

$$S + O_2 = SO_2\ ; \qquad 2S + 3O_2 = 2SO_3$$

(ii) *Action on hydrogen :* When a mixture of hydrogen and sulphur vapour is passed over red hot pumice stones or when hydrogen is passed through molten sulphur, *hydrogen sulphide* is produced.

$$H_2 + S = H_2S$$

(iii) *Action on chlorine :* When chlorine is bubbled through *boiling* sulphur, *sulphur monochloride* —an orange liquid is produced.

$$2S + Cl_2 = S_2Cl_2$$

(iv) *Action on phosphorus :* Sulphur reacts with phosphorus at ordinary temperatures yielding *phosphorus penta sulphide.*

$$P_4 + 10S = 2P_2S_5$$

(v) *Action on carbon :* On passing sulphur vapour over red hot carbon, *carbon di-sulphide* is prduced.

$$C + 2S = CS_2$$

2. **Action on metals :**

Heated metals like *copper, zinc, iron, sodium* etc., react with sulphur yielding the corresponding sulphides.

$$Cu + S = CuS\ (\text{black})\ ; \qquad Fe + S = FeS\ (\text{black})$$

Sodium or *potassium* catches fire as soon as it comes in contact with sulphur vapour.

$$2Na + S = Na_2S$$

At an ordinary temperature *mercury combines with sulphur* when powdered sulphur is triturated with mercury yielding *mercuric sulphide.*

$$Hg + S = HgS$$

3. **Action on mineral acids.**

(i) Sulphur *does not react with dilute H_2SO_4,* or *dilite HNO_3* or *conc. HCl.*

(ii) When sulphur is treated with *hot and conc. H_2SO_4,* it is oxidised to SO_2 and H_2SO_4 is reduced to SO_2.

$$\begin{array}{c} 2H_2SO_4 = 2H_2O + 2SO_2 + 2O \\ S + 2O = SO_2 \\ \hline 2H_2\overset{+6}{S}O_4 + \overset{0}{S} = 3\overset{+4}{S}O_2 + 2H_2O \end{array}$$

(iii) With *hot and conc. HNO_3* sulphur is oxidised to *sulphuric acid,* nitric acid being reduced to NO_2.

$$\begin{array}{c} (2HNO_3 = H_2O + 2NO_2 + O) \times 3 \\ S + 3O = SO_3 \\ H_2O + SO_3 = H_2SO_4 \\ \hline 6H\overset{+5}{N}O_3 + \overset{0}{S} = H_2\overset{+6}{S}O_4 + 6\overset{+4}{N}O_2 + 2H_2O \end{array}$$

4. **Action on alkali.**

Sulphur dissolves in *hot and concentrated solution of strong alkalis* [NaOH, KOH, $Ca(OH)_2$] with the formation of metallic *sulphides* and *thiosulphates.* The sulphides further combine with excess of sulphur yielding *poly sulphides.*

$$4S + 6NaOH = 2Na_2S + Na_2S_2O_3 + 3H_2O$$
$$Na_2S + 4S = Na_2S_5$$
$$12S + 3Ca(OH)_2 = 2CaS_5 + CaS_2O_3 + 3H_2O$$

5. **Action on metallic sulphites.**

When a solution of *sodium* or *potassium sulphite* is boiled with powdered sulphur, *thiosulphate* is produced.

$$Na_2SO_3 + S = \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3}$$

6. **Action on oxidising agents.**

Sulphur *ignites with explosion* when it is heated with oxidising agents like $KClO_3$, KNO_3 etc.

$$2KNO_3 = 2KNO_2 + 2O$$
$$S + 2O = SO_2$$

7. *Potassium carbonate* on being treated *with excess of sulphur,* a mixture of *polysulphide* and *thiosulphate* is obtained. This brown coloured substance is called *Liver of Sulphur.*

$$6S + 3K_2CO_3 = 2K_2S_2 + K_2S_2O_3 + 3CO_2$$

- **Tests** (i) Sulphur is insoluble in water but soluble in CS_2.

(ii) Sulphur does not dissolve in conc. HCl and in dilute H_2SO_4 or HNO_3.

(iii) Sulphur burns with *a blue flame in air* producing sulphur di-oxide which is colourless and a pungent smelling gas. When this gas is passed through acidified $K_2Cr_2O_7$ solution, it turns green.

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + \underset{\text{(Green)}}{Cr_2(SO_4)_3} + H_2O$$

• **Uses :** (i) Sulphur is largely used in the preparation of sulphur di-oxide which is used in the manufacture of H_2SO_4. (ii) It is used in the preparation of calcium bisulphite which is used in the paper industry. (iii) It is also used to prepare CS_2, S_2Cl_2 (used as solvents), sodium thiosulphate (used in photography), ultramarine (used as pigments). (iv) It is used as fungicide in agriculture and as a disinfactant. Colloidal sulphur and milk of sulphur are used as medicines.

• **To prove that different allotropes of sulphur belong to the same element.**

(a) When a fixed amount of each of the different allotropes of sulphur in pure state, is separately burnt in pure and dry O_2, each of them is found to give sulphur di-oxide only. It has been found that the same amount of any allotrope of sulphur produces the same amount of SO_2. Thus it is proved that all the allotropes of sulphur consist of the same element. $S + O_2 = SO_2$

(b) A definite weight of each of the different allotropes of sulphur in pure state is taken in a beaker and is mixed with fuming nitric acid. The beaker is then heated on a sand bath. Sulphur is oxidised to sulphuric acid. The solution thus obtained is cooled and diluted with excess of distilled water and boiled again. After cooling $BaCl_2$ solution is added to it till barium sulphate is completely precipitated. The produced $BaSO_4$ is collected by filtration and washed with distilled water and then dried in a desiccator. It is found that the same weight of different allotropes of sulphur produces the same amount of $BaSO_4$. Thus it is experimentally proved that different allotropes of sulphur contain the same element, i.e., sulphur.

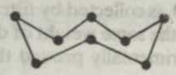
$$S + 6HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O$$
$$H_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2HCl$$

• **At an ordinary temperature oxygen is a colourless gas while sulphur is a pale yellow solid —Explain why.**

Oxygen molecule is diatomic and two oxygen atoms are covalently linked together to form O_2 molecule. In oxygen molecule the attraction between its individual molecules is very weak and that is why O_2 is a gas at an ordinary temperature. The atomicity of sulphur depends on the temperature. At an ordinary temperature sulphur molecule consists of eight atoms which are covalently linked together to form a puckered octahedral ring. Due to such structure of sulphur molecule, its molecular weight becomes high and as a result it is solid at ordinary temperature.

• Comparison of the properties of sulphur and oxygen :

Properties	Oxygen (O_2)	Sulphur (S_8)
Similarities		
(1) Position in the in the periodic table	Occupies group VIB of the second period in the periodic table, valence electrons being $2s^2 2p^4$	Occupies group VIB of the third period in the periodic table—valence electrons being $3s^2 3p^4$
(2) Occurrence	Occurs in free state in nature.	Occurs in free state in nature.
(3) Allotropy	Exhibits allotropy. O_3 is the allotropic modification of oxygen	Exhibits allotropy. Sulphur exists both in cystalline and amorphous allotropic forms
(4) Catenation property	Oxygen has the catenation property which is exhibited in H_2O_2. H—O—O—H	Sulphur also exhibits the catenation property as in H_2S_2. H—S—S—H
(5) Hydrides	Has got two hydrides—H_2O and H_2O_2. H_2O is neutral.	Has got two hydrides—H_2S and H_2S_2. H_2S is a weak acid.
(6) Action on metals	Combines with metals producing basic oxides. These oxides produce alkalis when dissolved in water	Combines with metals producing metallic sulphides. These sulphides when dissolved in acid produce H_2S.
(7) Action on non-metals	Produces acidic oxides which yield acids on treatment with water e.g., $C + O_2 = CO_2$. $CO_2 + H_2O = H_2CO_3$. Carbon di-oxide reacts with alkalis to produce carbonate salts.	Produces sulphides e.g., $C + 2S = CS_2$. Carbon di-sulphide reacts with alkalis to produce thiocarbonate. $3CS_2 + 6NaOH = 2Na_2CS_3 + Na_2CO_3 + 3H_2O$

Properties	Oxygen (O_2)	Sulphur (S_8)
Dissimilarities.		
(1) Physical state	O_2 is a colourless gas at ordinary temperature	Sulphur is a pale yellow solid
(2) Oxidation number	Oxygen exhibits mainly (−2) oxidation state and other oxidation states exhibited by O_2 are (+2) and (−1)	Sulphur exhibits variable oxidation states e.g., (−2), (+4), (+6)
(3) Combustibility	It is not combustible but supports combustion.	Sulphur itself is combustible in air and forms SO_2 and SO_3.
(4) Action on conc. HNO_3	Does not react with HNO_3	Reacts with conc. HNO_3 with the formation of H_2SO_4
(5) Molecular structure	Diatomic and linear $:\ddot{O}=\ddot{O}:$	Sulphur molecule consists of 8 atoms having octagonal structure 

• Comparison between the properties of sulphur and oxygen :

(A) Similarities :—

Both sulphur and oxygen belong to group VIB of the periodic table. So they exhibit similarities in their properties.

(i) Both sulphur and oxygen are found to occur in free state in nature.

(ii) Both have a similar electronic configurations with six valence electrons in their outermost orbits.

Oxygen—$1s^2\ 2s^2\ 2p^4$ Sulphur—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

(iii) Both the elements exihibit allotropy. —O_3 is the allotrope of O_2. Sulphur exists both in the crystalline and amorphous forms.

(iv) Both sulphur and oxygen form similar compounds.

For example—

With carbon—carbondioxide (CO_2), carbon disulphide (CS_2)

With phosphorus—phosphorus pentoxide (P_2O_5), phosphorus penta sulphide (P_2S_5)

With hydrogen—water (H_2O), hydrogen sulphide (H_2S)

(vi) Both of them combine with metals—oxygen forms metallic oxides and sulphur forms metallic sulphides. Oxides and sulphides exhibits similar properties e.g.

$$FeO + 2HCl = FeCl_2 + H_2O$$

$$FeS + 2HCl = FeCl_2 + H_2S$$

Points of dissimilarity.

(i) *State*—Oxygen is a colourless and odourless gas at an ordinary temperature but sulphur is a pale yellow solid.

(ii) *Occurrence*—Oxygen is more widely distributed in nature than sulphur.

(iii) *Atomicity*—Oxygen is diatomic and the two oxygen atoms are joined covalently to form the molecule but the atomicity of sulphur molecule depends on the temperature. At ordinary temperature sulphur molecule consists of eight atoms which are joined covalently to form a puckered octahedral ring.

(iv) *Oxidation number*—Oxygen in general exihibits the (−2) oxidation state. It can exhibit (+2) and (−1) oxidation states also. But sulphur exhibits variable oxidation states e.g., (−2), (+4), (+6).

(v) *Combustibility*—Sulphur is combustible and burns with a blue flame while oxygen is not combustible but is a supporter of combustion.

(vi) *Hydrides*—The main hydride of oxygen is water (H_2O) which is a colourless and odourless liquid at an ordinary temperature and is a neutral oxide. The hydride of sulphur (H_2S) is a colourless gas having the smell of rotten eggs. It is acidic in nature.

(vii) *Reducing property*—Sulphur reduces conc. HNO_3 to oxides of nitrogen while oxygen cannot reduce HNO_3.

(viii) *Electronegativity*— Oxygen is strong electronegative element, while sulphur is weak electronegative element.

HYDRIDE OF SULPHUR.

• Hydrogen Sulphide or Sulphuretted hydrogen •

Formula—H_2S	**Molecular weight : 34**

Hydrogen sulphide is the main and important hydride of sulphur. It is found to occur in volcanic gases. It is present in small amounts in spring water. This gas is produced by the decay and decomposition of organic matters, having sulphur. Air contains traces of this gas.

6.5. Preparation of hydrogen sulphide in the laboratory.

[A] **Principle :** Hydrogen sulphide is prepared by the action of *cold and dilute sulphuric acid* on *ferrous sulphide.*

$$FeS + H_2SO_4 = FeSO_4 + H_2S \uparrow$$

[B] **Procedure :** Small pieces of ferrous sulphide are taken in a Woulfe's bottle fitted with a thistle funnel and a delivery tube. The end of the thistle funnel reaches almost the bottom of the Woulfe's bottle. The end of the delivery tube is introduced into an upright dry gas jar. Now dilute sulphuric acid is added to the ferrous sulphide in the Woulfe's bottle through the thistle funnel. The lower end of the thistle funnel and ferrous sulphide are kept under the surface of acid. As soon as FeS comes in contact with the acid, hydrogen sulphide begins to evolve. It passes through the delivery tube. As hydrogen sulphide is heavier than air, it is collected in a gas jar by the upward displacement of air.

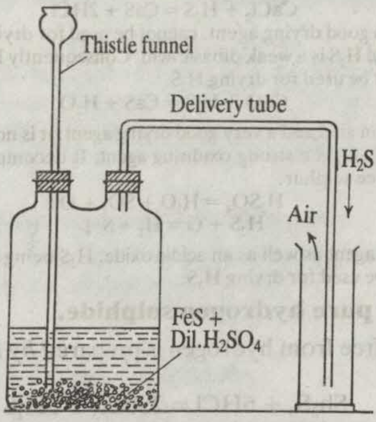


Fig. 6.11 : Preparation of H_2S

As the gas is much less soluble in hot water it may be collected over hot water.

[C] **Purification** : The H_2S gas thus prepared contains *hydrogen, moisture,* and hydrogen chloride gas (if H_2S is prepared by the action of HCl on FeS).

The free hydrogen is produced by the action of dil. H_2SO_4 or HCl on metallic iron present in FeS. The gas is purified by passing it at first through a *saturated solution of sodium hydrogen sulphide* to remove the HCl vapours.

$$NaHS + HCl = NaCl + H_2S.$$

The gas is then passed through a U tube containing *phosphorus pentoxide* which absorbs moisture. The gas, freed from HCl and moisture is then cooled by dry-ice when H_2S becomes liquid. The uncondensed hydrogen is pumped out. This liquid H_2S is converted to gas at room temperature.

- **Nitric acid or conc. H_2SO_4 is not used in the preparation of H_2S in the laboratory.**

(i) Nitric acid is not used in the preparation of H_2S from metallic sulphides. This is because of the fact that the H_2S produced by the action of HNO_3 on FeS, is oxidised to sulphur due to the oxidising action of nitric acid. So instead of H_2S, a yellow precipitate of sulphur is obtained.

$$\begin{array}{c} FeS + 2HNO_3 = Fe(NO_3)_2 + H_2S \\ 2HNO_3 = H_2O + 2NO_2 + O \\ H_2S + O = H_2O + S \\ \hline FeS + 4HNO_3 = Fe(NO_3)_2 + 2NO_2 + S \downarrow + 2H_2O \end{array}$$

(ii) Conc. H_2SO_4 is also unsuitable for the preparation of H_2S from metallic sulphides. Conc. H_2SO_4 reacts with FeS to produce $FeSO_4$ and H_2S, but due to the oxidising action of conc. H_2SO_4 the produced H_2S is oxidised to yellow sulphur.

$$\begin{array}{c} H_2SO_4 + FeS = FeSO_4 + H_2S \\ H_2SO_4 = H_2O + SO_2 + O \\ H_2S + O = H_2O + S \\ \hline FeS + 2H_2SO_4 = FeSO_4 + SO_2 + S + 2H_2O \end{array}$$

- **H_2S cannot be dried by $CaCl_2$ or CaO or conc. H_2SO_4 but can be dried by P_2O_5.**

(i) H_2S is a weak dibasic acid and so it reacts with $CaCl_2$ to produce CaS and HCl.

$$CaCl_2 + H_2S = CaS + 2HCl$$

Thus fused $CaCl_2$ though a good drying agent, cannot be used for drying H_2S.

(ii) CaO is a basic oxide and H_2S is a weak dibasic acid. Consequently H_2S reacts with CaO to form CaS and water. Thus CaO cannot be used for drying H_2S.

$$CaO + H_2S = CaS + H_2O$$

(iii) Conc. H_2SO_4 though an acid and a very good drying agent, it is not suitable for drying H_2S. This is due to the fact that conc. H_2SO_4 is a strong oxidising agent. It decomposes to give off nascent oxygen which oxidises H_2S to give free sulphur.

$$\begin{array}{c} H_2SO_4 = H_2O + SO_2 + O \\ H_2S + O = H_2 + S \downarrow \end{array}$$

(iv) P_2O_5 is a good drying agent as well as an acidic oxide. H_2S being a weak acid, does not react with P_2O_5. Thus P_2O_5 can safely be used for drying H_2S.

• Preparation of pure hydrogen sulphide.

Hydrogen sulphide free from hydrogen is prepared *by heating antimony sulphide with conc. HCl.*

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

The evolved gas is passed through a wash bottle containing water which removes hydrogen chloride. Then it is passed over phosphorus pentoxide to remove moisture.

6.6. Other methods of preparation of H_2S.

1. From metallic sulphides : Metallic sulphides on being treated with *dilute hydrochloric or sulphuric acid* evolves hydrogen sulphide.

$$\begin{array}{c} Na_2S + 2HCl = 2NaCl + H_2S \\ CaS + 2HCl = CaCl_2 + H_2S \end{array}$$

2. H_2S may also be prepared by the action of *nascent hydrogen* ($Zn + H_2SO_4$) on non metallic sulphides.

$$As_2S_3 + 12H = 2AsH_3 + 3H_2S$$

3. Preparation of hydrogen sulphide in Kipp's apparatus :

Hydrogen sulphide, for intermittent use in qualitative analysis is prepared in Kipp's apparatus. The description of Kipp's apparatus and its working principle have already been discussed in the preparation of hydrogen in chapter I.

Pieces of ferrous sulphide are placed in the central globe. The stop-cock is opened and dilute H_2SO_4 is poured down the funnel attached to the upper globe until the FeS pieces are covered by the acid. As soon as the acid comes in contact with FeS, H_2S begins to evolve. When the stop-cock is closed the gas produced by the action of FeS on H_2SO_4 pushes the acid into the upper globe. As a result FeS ceases to be in contact with the acid and the reaction stops, but the gas remains in the central globe ready for use.

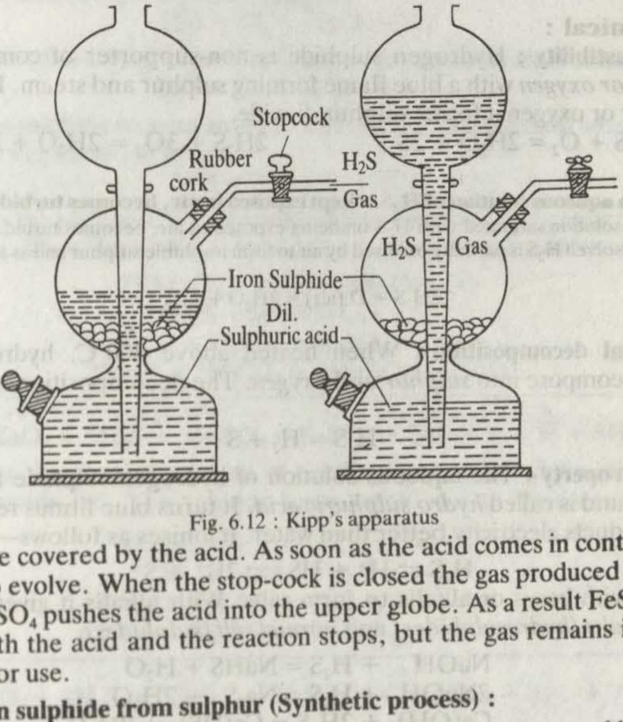


Fig. 6.12 : Kipp's apparatus

4. Hydrogn sulphide from sulphur (Synthetic process) :

Hydrogen sulphide may also be obtained by passing a mixture of hydrogen and *sulphur vapours* over a *nickel catalyst* heated to 450°C.

$$H_2 + S = H_2S$$

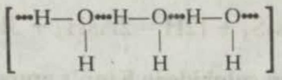
6.7. Properties of hydrogen sulphide.

[A] **Physical :**

(i) Hydrogen sulphide is a colourless gas having an unpleasant smell resembling that of rotten eggs. (ii) It is fairly soluble in cold water but not in hot water. (iii) It is heavier than air. (iv) It can easily be converted to a colourless liquid by cooling it to −60.7°C or by applying strong pressure. (v) The gas is highly poisonous.

• Oxygen is a gas and sulphur is a solid, but at room temperature the hydride of oxygen (H_2O) is a liquid and the hydride of sulphur is a gas—explain why.

H_2O is a liquid and H_2S is a gas at ordinary temperature. This is because of the fact that oxygen is a strong electronegative element than S, and the size of O atom is much less than that of S atom, as a result hydrogen bond is produced between the H atom of one H_2O molecule and O atom of another molecule forming a chain of water molecules, i.e. ;



$$\left[\begin{array}{l}\cdots H-O\cdots H-O\cdots H-O\cdots \\ \qquad\;\; | \qquad\quad\;\; | \qquad\quad\;\; | \\ \qquad\;\; H \qquad\quad\; H \qquad\quad\; H\end{array}\right]$$

Water molecules associate through hydrogen bonding. Thus the water molecules exist as polymeric molecule. Much heat energy is required to break the H bonds of water to bring the molecules in monomeric form. So water is liquid at ordinary temperature and its boiling point is higher than that of H_2S. On the other hand due to the large size and small electronegativity of S atom, H_2S cannot form hydrogen bond. So H_2S molecules exist as single molecule. The H_2S molecules are attracted by each other only by Vander Waals force which is very weak. For this reason H_2S is a gas at ordinary temperature and its b.p. is much less than that of H_2O.

[B] Chemical :

1. Combustibility : Hydrogen sulphide is non-supporter of combustion but it *burns in air or oxygen* with a blue flame forming sulphur and steam. In the presence of excess air or oxygen it forms sulphur dioxide.

$$2H_2S + O_2 = 2H_2O + 2S\downarrow \qquad 2H_2S + 3O_2 = 2H_2O + 2SO_2\uparrow$$

- **When an aqueous solution of H_2S is kept exposed in air, becomes turbid—explain why.**

An aqueous solution saturated with H_2S on being exposed to air, becomes turbid. This is due to the fact that the dissolved H_2S is partially oxidised by air to form insoluble sulphur and as a result the solution turns turbid.

$$2H_2S + O\,(\text{air}) = 2H_2O + 2S\downarrow$$

2. Thermal decomposition : When heated above 400°C, hydrogen sulphide begins to decompose into *sulphur* and *oxygen*. The decomposition is completed at 1700°C.

$$H_2S = H_2 + S$$

3. Acid Property : The aqueous solution of hydrogen sulphide acts as a weak dibasic acid and is called *hydro sulphuric acid*. It turns blue litmus red. Its aqueous solution conducts electricity better than water. It ionises as follows—

$$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2H^+ + S^=$$

It reacts with bases or alkalis to form salts. With alkalis it gives two series of salts—*acid salts (hydrosulphides)* and *normal salt (sulphides)*.

$$\begin{aligned}&NaOH &&+ H_2S = NaHS + H_2O\\ &2NaOH &&+ H_2S = Na_2S + 2H_2O\\ &Ca(OH)_2 &&+ 2H_2S = Ca(HS)_2 + 2H_2O\\ &Ca(OH)_2 &&+ H_2S = CaS + 2H_2O\end{aligned}$$

Metals which are above hydrogen in the electro-chemical series displace hydrogen from hydrogen sulphide at elevated temperatures with the formation of the corresponding sulphides.

$$Pb + H_2S = PbS + H_2, \qquad 2Na + H_2S = Na_2S + H_2$$

Mercury, silver are placed below hydrogen in the electro chemical series, yet the metals liberate H_2 from H_2S with the formation of the corresponding sulphides. This is because of the fact that HgS or Ag_2S are highly stable compounds. When H_2S is made to react with these metals, the oxidation potentials of Hg and Ag are increased considerably making them very easily oxidisable to Hg^{++} and Ag^+ respectively. Hence in presence of $S^=$ ion Hg or Ag can reduce H^+, though hydrogen is placed above them in the electro chemical series.

$$Hg + H_2S = HgS + H_2\uparrow, \qquad 2Ag + H_2S = Ag_2S + H_2\uparrow$$

4. Reducing Property : Hydrogen sulphide acts as a strong reducing agent as the $S^=$ ion in hydrogen sulphide readily gives up electrons to the oxidising agents to form sulphur atom.

$$H_2S \rightleftharpoons 2H^+ + S^=, \qquad S^= - 2e \rightarrow S$$

(a) *Reduction of ferric salts.* It reduces yellow solution of ferric salt to colourless solution of ferrous salt, itself being oxidise to sulphur.

$$2\overset{+3}{Fe}Cl_3 + H_2S = 2\overset{+2}{Fe}Cl_2 + 2HCl + S\downarrow$$

$$\overset{+3}{Fe_2}(SO_4)_3 + H_2S = 2\overset{+2}{Fe}SO_4 + H_2SO_4 + S\downarrow$$

(b) Hydrogen sulphide reduces *chlorine water* to *hydrochloric acid,* itself being oxidised to give a yellow precipitate of sulphur.

$$H_2S + Cl_2 = 2HCl + S\downarrow$$

(c) Red coloured *bromine water* is reduced to colourless *hydrobromic acid.*

$$H_2S + Br_2 = 2HBr + S\downarrow$$

(d) Hydrogen sulphide reduces *iodine to colourless hydroiodic acid* when it is passed through iodine suspended in water.

$$H_2S + I_2 = 2HI + S\downarrow$$

(e) It reduces the pink solution of acidified *potassium permanganate* to colourless *manganous salt.* The solution turns turbid due to the formation of free *sulphur.*

$$\begin{array}{c}
2KMnO_4 = K_2O + 2MnO + 5O \\
5H_2S + 5O = 5H_2O + 5S \\
K_2O + H_2SO_4 = K_2SO_4 + H_2O \\
2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O \\
\hline
2K\overset{+7}{Mn}O_4 + 5H_2\overset{-2}{S} + 3H_2SO_4 = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 5\overset{0}{S} + 8H_2O
\end{array}$$

(f) It reduces the orange solution of acidified *patassium dichromate* to green solution of *chromic salt.* The solution turns turbid due to the formation of free sulphur.

$$\begin{array}{c}
K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O \\
3H_2S + 3O = 3H_2O + 3S \\
K_2O + H_2SO_4 = K_2SO_4 + H_2O \\
Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O \\
\hline
K_2\overset{+6}{Cr_2}O_7 + 3H_2\overset{-2}{S} + 4H_2SO_4 = K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + 3\overset{0}{S}\downarrow + 7H_2O
\end{array}$$

(g) *Moist sulphur dioxide* is reduced by H_2S to free *sulphur.*

$$\overset{+4}{S}O_2 + 2H_2S = 2H_2O + 3\overset{0}{S}$$

This reaction proves that H_2S is stronger reducing agent than SO_2.

(h) Concentrated *nitric acid* and *sulphuric acid* are reduced to *nitrogen dioxide* and *sulphur dioxide* respectively.

$$\begin{array}{c}
2HNO_3 = H_2O + NO_2 + O \\
H_2S + O = H_2O + S \\
\hline
2H\overset{+5}{N}O_3 + H_2S = 2H_2O + S + \overset{+4}{N}O_2
\end{array}$$

$$\begin{array}{c}
H_2SO_4 = H_2O + SO_2 + O \\
H_2S + O = H_2O + S \\
\hline
H_2\overset{+6}{S}O_4 + H_2\overset{-2}{S} = 2H_2O + \overset{+4}{S}O_2 + \overset{0}{S}
\end{array}$$

(i) *Hydrogen peroxide* is reduced to *water*.

$$H_2\overset{-1}{O}_2 + H_2\overset{-2}{S} = 2H_2\overset{-2}{O} + \overset{0}{S}$$

- **H_2S can reduce only but cannot oxidise—explain why :**

The oxidation number of S atom in H_2S is (−2). This is the lowest oxidation state of S in its compounds. The next higher oxidation number of S is 0. Consequently the S atom of H_2S has no scope to decrease its oxidation number any further i.e., it cannot be reduced. This is why H_2S can never act as an oxidising agent. On the other hand the S atom of H_2S has the scope to increase its oxidation number from −2 to 0 or to (+4). Thus it can be oxidised. This oxidation of S atom can only be brought out by reducing other substance. So H_2S cannot behave as an oxidant but can act as a reductant.

5. Formation of thionic acid. At 0°C, hydrogen sulphide reacts with an aqueous solution of SO_2 with the formation of *thionic acid.*

$$5H_2S + 10SO_2 = \underset{\text{Penta thionic acid}}{3H_2S_5O_6} + 2H_2O$$

6. *Sulphur is precipitated* when H_2S is passed through an *aqueous solution of sodium bisulphite.*

$$NaHSO_3 + 2H_2S + HCl = NaCl + 3S\downarrow + 3H_2O$$

7. **Precipitation of sulphides.**

The sulphides of many metals are precipitated when hydrogen sulphide is passed through the aqueous solution of their salts.

$$CuSO_4 + H_2S = \underset{\text{black ppt}}{CuS\downarrow} + H_2SO_4$$

$$Pb(NO_3)_2 + H_2S = \underset{\text{black ppt}}{PbS\downarrow} + 2HNO_3$$

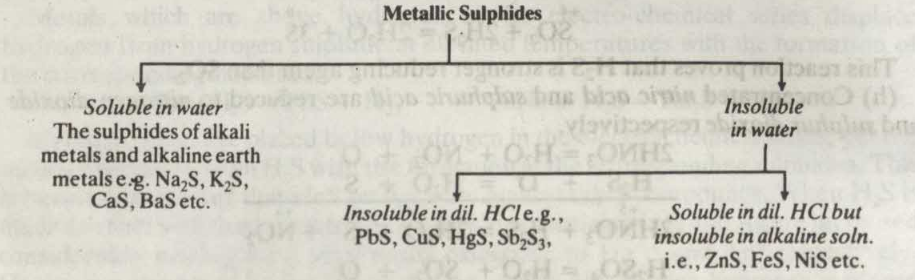
$$ZnSO_4 + H_2S = \underset{\text{white ppt}}{ZnS\downarrow} + H_2SO_4$$

$$CdCl_2 + H_2S = \underset{\text{yellow ppt}}{CdS\downarrow} + 2HCl$$

6.8. The use of hydrogen sulphide as a reagent in the qualitative analysis of metallic salts.

Hydrogen sulphide is used as an important reagent for the detection of basic radicals in qualitative analysis.

The use of H_2S as a reagent for the detection of basic radicals is based on the solubilities of different metallic sulphides in different media. For the qualitative analysis, the metallic sulphides may be classified as follows according to their solubilities in different media.


Metallic Sulphides
Soluble in water
The sulphides of alkali metals and alkaline earth metals e.g. Na_2S, K_2S, CaS, BaS etc.
Insoluble in water
Insoluble in dil. HCl e.g., PbS, CuS, HgS, Sb_2S_3,
Soluble in dil. HCl but insoluble in alkaline soln. i.e., ZnS, FeS, NiS etc.

(i) Metallic sulphides which are insoluble in dil. HCl are precipitated from their solutions acidified with dil. HCl.

When hydrogen sulphide is passed through the metallic salt solutions acidified with dil. HCl, the sulphides of the basic radicals are precipitated which are identified by their colours. These radicals are placed in Gr II of the qualitative analysis. These are Cu^{++}, Pb^{++}, Cd^{++}, Sb^{+++} etc.

$$CuSO_4 + H_2S = H_2SO_4 + CuS \downarrow \text{(black ppt)}$$

$$Pb(NO_3)_2 + H_2S = 2HNO_3 + PbS \downarrow \text{(black ppt)}$$

$$2SbCl_3 + 3H_2S = 6HCl + Sb_2S_3 \downarrow \text{(orange ppt)}$$

$$CdCl_2 + H_2S = 2HCl + CdS \downarrow \text{(yellow ppt)}$$

(ii) **Metallic sulphides which are soluble in acid medium but are insoluble in alkaline medium.**

Some metallic sulphides such as ZnS, FeS, NiS etc., are soluble in dil. HCl but insoluble in solution made alkaline by adding ammonium hydroxide. Thus the sulphides of Zn, Fe, Co, Mn etc., are precipitated when H_2S gas is passed through the solutions of these salts in alkaline medium, which are identified by their colours. These radicals are placed in group IIIB of the qualitative analysis.

$$ZnSO_4 + H_2S = H_2SO_4 + ZnS \downarrow \text{(white ppt)}$$

$$FeCl_2 + H_2S = 2HCl + FeS \downarrow \text{(black ppt)}$$

$$MnSO_4 + H_2S = H_2SO_4 + MnS \downarrow \text{(pink ppt)}$$

(iii) **The metallic sulphides which are soluble in water :**

The metals whose sulphides are soluble in water, are not precipitated by H_2S e.g., Na_2S, K_2S etc.

• Depending on the different solubilities of the metallic sulphides in different media, the metallic radicals can be separated from a mixture of their salts.

As for example, a mixture is there which contains aqueous solutions of $CuSO_4$, $ZnSO_4$ and Na_2SO_4. The mixture is dissolved in dil. HCl and H_2S is passed through the acidified solution of the mixture, when CuS (black) being insoluble in HCl will get precipitated. The black precipitate of CuS is filtered off.

The filtrate is then boiled to remove H_2S and is made alkaline by adding ammonium hydroxide. Hydrogen sulphide is passed through this alkaline solution when a white precipitate of ZnS is obtained. It is separated by filtration and the resulting filtrate contains sodium salt only. Thus H_2S helps to separate metallic radicals from solution of their salts.

• Tests of hydrogen sulphide :

(i) Hydrogen sulpide has a characteristic unpleasant smell resembling that of rotten eggs.

(ii) It turns of *lead acetate* paper black due to the formation of lead sulphide.

$$(CH_3COO)_2Pb + H_2S = 2CH_3COOH + PbS \downarrow \text{(black)}$$

(iii) Hydrogen sulphide does not change the colour of sodium nitroprusside, but when H_2S is passed through **freshly prepared alkaline sodium nitroprusside** solution, a violet colouration is produced due to the formation of a complex salt.

$$\underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} + H_2S + 2NaOH = \underset{\text{Complex salt of violet colour}}{Na_4[Fe(CN)_5NOS]} + 2H_2O$$

• Tests for sulphides :

Dry test : The metallic sulphide is taken in a test tube and dil. H_2SO_4 is added to it and the mixture is heated. A colourless gas having the smell of rotten eggs is found to evolve. When a paper soaked in lead acetate solution is held in the gas, the paper turns black.

Wet test : (i) $AgNO_3$ solution is added to the aqueous solution of the metallic sulphide when a black precipitate of Ag_2S is obtained, which is soluble in dil. HNO_3.

(ii) The aqueous solution of a metallic sulphide is made alkaline by adding NaOH solution. Then few drops of sodium nitroprusside is added to it, when the solution turns violet.

$$Na_2[Fe(CN)_5NO] + Na_2S = \underset{\text{violet colour}}{Na_4[Fe(CN)_5NOS]}$$

- **Uses :** (i) H_2S is used in the preparation of polysulphides.

(ii) It is also used as a regent for the detection of basic radicals in qualitative analysis.

- **Prove that hydrogen sulphide contains sulphur and hydrogen :**

Sulphur : A lighted taper is introduced in a jar of hydrogen sulphide. The taper is extinguished but the gas continues to burn with a blue flame. After the completion of the reaction a yellow residue is found to depositon the inner walls of the gas jar. It is collected and a portion of it is added to carbon di-sulphide—it is found to dissolve in CS_2. The other portion of the solid is burnt in air when a colourless gas is produced having a suffocating smell of burning sulphur and which turns a paper soaked in acidified potassium dichromate solution green. So the colourless gas is nothing but SO_2 which is formed by the burning of the yellow solid in air. Thus it is conclusively proved that the yellow solid is sulphur and this sulphur has come from hydrogen sulphide

$$2H_2S + O_2 = 2H_2O + 2S \downarrow \qquad S + O_2 = SO_2$$

Hydrogen : A thumb tube is filled with mercury and its mouth is dipped in mercury in a trough. A small volume of pure and dry hydrogen sulphide is collected into the tube over mercury. A piece of tin foil is introduced into the horizontal part of the tube. The tin foil is now heated in the atmosphere of hydrogen sulphide when it reacts with hydrogen sulphide producing a solid product (SnS) and a colourless gas. The residual gas inside the tube burns in air with a blue flame producing a colourless liquid which turns anhydrous $CuSO_4$ blue. Thus it is proved that the colourless liquid is water which is formed by its combination with O_2 of air. So the colourless gas is H_2 and this H_2 has come from hydrogen sulphide.

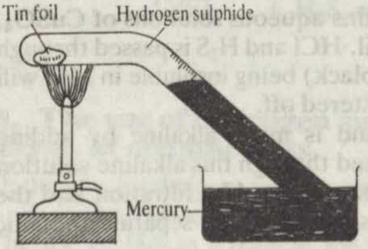


Fig 6.13 :

$$H_2S + Sn = SnS + H_2$$
$$2H_2 + O_2 = 2H_2O$$

- **Prove that hydrogen sulphide is a reducing agent.**

1. An acidified solution of potassium permanganate is taken in a test tube and hydrogen sulphide is passed through the solution. It is observed that the pink colour of the potassium permanganate solution becomes colourless and a yellow precipitate of sulphur is obtained. This is due to the fact that H_2S reduces potassium permanganate to colourless manganous salt.

$$2K\overset{+7}{Mn}O_4 + 5H_2\overset{-2}{S} + 3H_2SO_4 = K_2SO_4 + 2\overset{+2}{Mn}SO_4 \mp 5\overset{0}{S} + 8H_2O$$

2. Potassium dichromate solution acidified with dil. H_2SO_4 is taken in a test tube and hydrogen sulphide is passed through it. It is observed that the orange colour of potassium dichromate turns green. This is due to the fact that hydrogen sulphide has reduced $K_2Cr_2O_7$ to green coloured chromic salt.

$$K_2\overset{+6}{Cr_2}O_7 + 3H_2\overset{-2}{S} + 4H_2SO_4 = K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + 3\overset{0}{S} + 7H_2O$$

• Prove that hydrogen sulphide is slightly soluble in water and its aqueous solution is acidic in nature.

A dry test tube is filled with hydrogen sulphide and is inverted on water in a beaker. Water is found to rise up the test tube slowly. A blue litmus paper is introduced into the solution of the test tube—the litmus paper turns red. Thus it is proved that H_2S is slightly soluble in water and its aqueous solution is acidic in nature.

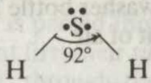
• How would you obtain H_2S from a metallic sulphate ?

A small amount of a sulphate salt is taken in the cavity on a charcoal block and is heated strongly in the reducing flame by means of blow pipe. The resulting mass is then treated with dil. HCl. Hydrogen sulphide is found to evolve which is identified by its unpleasant smell of rotten eggs.

The sulphate salt is at first reduced by the carbon particles to form sulphide. This sulphide on treatment with dil. HCl evolves H_2S.

$$Na_2SO_4 + 4C = Na_2S + 4CO \uparrow$$
$$Na_2S + 2HCl = 2NaCl + H_2S \uparrow$$

• Structure : Like H_2O, H_2S also have a bent structure with H—S bond length = 1·35Å. and H—S—H bond angle = 92°.



• Sulphides : *A sulphide is a compound of two elements one of which is sulphur.*

Preparation : (1) *By the reduction of metallic sulphates :* Metallic sulphates on being reduced by carbon at high temperature yield sulphide salts.

$$BaSO_4 + 4C = BaS + 4CO$$

(ii) *Metallic hydroxides* on being treated with H_2S yield sulphides.

$$2NaOH + H_2S = Na_2S + 2H_2O$$

(iii) When H_2S gas is passed through an aqueous solution of metallic salt corresponding sulphides are produced.

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

• Sulphur di-oxide •

Formula—SO_2	**Molecular weight : 64**

Sulphur dioxide was first prepared by *Priestly* in 1771 by heating mercury in conc. H_2SO_4. It is also found in volcanic gases.

6.9. Preparation of sulphur dioxide.

(1) *Laboratory method.*

[A] **Principle :** Sulphur dioxide is prepared in the laboratory by heating *copper turnings* with *conc. H_2SO_4.* In this reactions *sulphuric acid is reduced by metallic copper to sulphur dioxide.*

$$\overset{0}{Cu} + 2H_2\overset{+6}{S}O_4 = \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + 2H_2O$$

[B] **Procedure :** (i) Some copper turnings are taken in a round bottomed flask fitted with a thistle funnel and a delivery tube. (ii) The end of the thistle funnel reaches almost the bottom of the flask. (ii) The flask is then clamped to a stand and is placed on a tripod stand on a wire gauze. (iv) The end of the delivery tube is introduced into a washer bottle containing conc. H_2SO_4. The washer bottle is fitted with another delivery tube the free end of which is introduced almost to the bottom of a gas gar. (v) Conc. H_2SO_4 is poured down the thistle funnel so that the end of it and the copper turnings remain dipped under the surface of the acid. (vi) The flask is then heated slowly when reaction takes place and sulphur dioxide is evolved. (vii) The evolved SO_2 passes through the washer bottle and the dried gas is collected in the gas jar by the upward displacement of air.

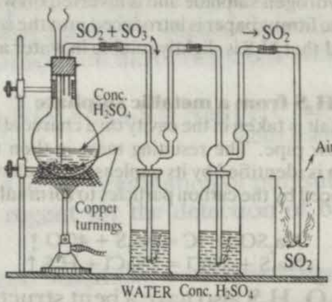


Fig. 6.14 : Preparation of SO_2

- **Lime cannot be used to dry SO_2 :**

Sulphur dioxide is an acidic oxide, while lime (CaO) is a basic oxide. Consequently lime reacts with SO_2 producing calcium sulphite. So it cannot be used to dry SO_2.

$$CaO + SO_2 = CaSO_3$$

SO_2 is fairly soluble in water at ordinary temperature, on the other hand it is heavier than air. In ordinary condition excepting moisture, it does not react with the other constituents of air. So SO_2 is collected by the upward displacement of air.

(2) *By the action of Ag, Hg, C, S etc. on conc. H_2SO_4*

Sulphur dioxide may also be obtained by the action of metals like *mercury, silver* and non metals like *carbon, sulphur* on conc. H_2SO_4.

$$\begin{aligned} 2Ag + 2H_2SO_4 &= Ag_2SO_4 + SO_2 + 2H_2O \\ Hg + 2H_2SO_4 &= HgSO_4 + SO_2 + 2H_2O \\ C + 2H_2SO_4 &= CO_2 + 2SO_2 + 2H_2O \\ S + 2H_2SO_4 &= 3SO_2 + 2H_2O \end{aligned}$$

(3) *From sulphites and bisulphites :*

At ordinary temperature sulphur dioxide may also be obtained by the action of *dilute HCl* or *dil. H_2SO_4 on sulphite* and *bisulphite salts.*

$$\begin{aligned} Na_2SO_3 + 2HCl &= 2NaCl + SO_2 + H_2O \\ Ca_2SO_3 + 2HCl &= 2CaCl_2 + SO_2 + H_2O \\ 2NaHSO_3 + H_2SO_4 &= Na_2SO_4 + 2SO_2 + 2H_2O. \end{aligned}$$

(4) *Preparation of SO_2 from sulphide ores :*

(i) During the extraction of metals like Cu, Pb, Zn etc., sulphur dioxide is obtained as a by-product when the sulphide ores of those metals are roasted i.e., heated in a current of air in a furnace. Thus sulphur dioxide is obtained by roasting zinc blend (ZnS), galena (PbS), copper pyrites (Cu_2S, Fe_2S_3).

$$2PbS + 3O_2 = 2PbO + 2SO_2\uparrow \qquad 2ZnS + 3O_2 = 2ZnO + 2SO_2\uparrow$$

$$Cu_2S, Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2\uparrow$$

(ii) Sulphur dioxide may also be obtained by roasting iron pyrites. It may also be obtained when sulphur is burnt in air or O_2.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2\uparrow \qquad S + O_2 = SO_2$$

6.10. Properties of sulphur dioxide.

[A] Physical :

(i) Sulphur dioxide is a colourless gas having a suffocating smell of burning sulphur. (ii) It is fairly soluble in water. (iii) It is nearly twice heavier than air. (iv) Sulphur dioxide can be converted to a colourless liquid by cooling it in a freezing mixture at an ordinary pressure.

[B] **Chemical properties :**

1. **Acidic properties.** (i) Sulphur dioxide is an acidic oxide. It dissolves in water with the formation of *sulphurous acid* which is dibasic and which turns blue litmus red. Sulphurous acid on being heated decomposes to give sulphur dioxide and water. *That is why sulphur dioxide is called anhydride of sulphurous acid.*

$$SO_2 + H_2O = H_2SO_3\ ; \qquad H_2SO_3 = H_2O + SO_2$$

(ii) It reacts with basic oxides to give *sulphites.*

$$CaO + SO_2 = CaSO_3\ ; \qquad MgO + SO_2 = MgSO_3$$

With alkalis it forms two types of salts–*normal salts* (sulphites) and *acid salts* (bisulphites).

$$2NaOH + SO_2 = Na_2SO_3\ ; \qquad Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3$$

(iii) When sulphur dioxide is passed through a solution of *sodium carbonate* or *potassium carbonate solution* at first their *sulphites* are formed with the liberation *of CO_2*. On passing excess SO_2 through the solution the produced sulphites are converted to *bisulphites.*

$$Na_2CO_3 + SO_2 = Na_2SO_3 + CO_2\uparrow\ ; \qquad Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3$$

(iv) *With lime water.* When sulphur dioxide is passed through *lime water,* at first *insoluble calcium sulphite* is formed and as a result the clear solution turns milky. On passing excess SO_2, soluble *calcium bisulphite* is produced and so the milkiness disappears.

$$Ca(OH)_2 + SO_2 = CaSO_3\downarrow + H_2O\ ; \qquad CaSO_3 + SO_2 + H_2O = Ca(HSO_3)_2$$

On boiling the calcium bisulphite solution, the *milkness reappears* due to the decomposition of calcium bisulphite into insoluble *calcium sulphite* and SO_2.

$$Ca(HSO_3)_2 = CaSO_3\downarrow + SO_2 + H_2O$$

2. **Combustibility :** Sulphur dioxide is not combustible neither a supporter of combustion, but the burning *sodium, potassium, magnesium, iron, carbon* etc., continue to burn in the gas. *Sodium or potassium burns in the gas to yield sulphite* and *thiosulphate.*

$$4Na + 3SO_2 = Na_2SO_3 + Na_2S_2O_3$$

Iron, magnesium burn in SO_2 with the formation of their *oxides* and *sulphites.*

$$3Fe + SO_2 = 2FeO + FeS\ ; \qquad 3Mg + SO_2 = 2MgO + MgS.$$

In these reactions, SO_2 is partly decomposed to give off nascent oxygen, at a high temperature produced by the burning metals. The evolved nascent oxygen supports the combustion of the metals and oxidises them.

$$\begin{array}{c} SO_2 = S + 2O \\ 2Fe + 2O = 2FeO \\ Fe + S = FeS \\ \hline 3Fe + SO_2 = 2FeO + FeS \end{array}$$

3. **Decomposition of SO_2 :** A saturated aqueous solution of SO_2 on being heated in a sealed tube at 150°C, sulphur separates out from the solution as a yellow precipitate. The precipitate dissolves in CS_2.

$$H_2O + SO_2 = H_2SO_3$$

$$3H_2\overset{+4}{S}O_3 = \overset{0}{S}\downarrow + 2H_2\overset{+6}{S}O_4 + H_2O$$

In this reaction, a part of H_2SO_3 is oxidised to H_2SO_4 and the other part is reduced to free sulphur. So it is a *disproportionation reaction.*

4. **Reducing property :** Sulphur dioxide is a *strong reducing agent.*

(i) When SO_2 is passed through *chlorine water,* Cl_2 is reduced to *hydrogen chloride* and SO_2 is oxidised to *sulphuric acid.*

$$SO_2 + H_2O = H_2SO_3 \;; \qquad Cl_2 + H_2\overset{+4}{S}O_3 + H_2O = 2H\overset{-1}{Cl} + H_2\overset{+6}{S}O_4$$

(ii) On passing SO_2 through *red coloured bromine* water, bromine is reduced to give *colourless hydrobromic acid,* SO_2 being oxidised to H_2SO_4.

$$\overset{0}{Br_2} + \overset{+4}{S}O_2 + 2H_2O = 2H\overset{-1}{Br} + H_2\overset{+6}{S}O_4$$

(iii) When SO_2 is passed through *iodine suspended in a water,* iodine dissolves to produce a *colourless* solution of *hydro iodic acid.*

$$\overset{0}{I_2} + \overset{+4}{S}O_2 + 2H_2O = 2H\overset{-1}{I} + H_2\overset{+6}{S}O_4$$

(iv) Sulphur dioxide reduces *ferric chloride* solution to *ferrous chloride* and as a result the colour of the solution changes from *yellow to colourless.*

$$2\overset{+3}{Fe}Cl_3 + \overset{+4}{S}O_2 + 2H_2O = 2\overset{+2}{Fe}Cl_2 + 2HCl + H_2\overset{+6}{S}O_4$$

(v) When sulphur dioxide gas is passed through the pink solution of *acidified potassium permanganate,* the later is reduced to give a colourless solution of *manganous salt.*

$$\begin{array}{c}
2KMnO_4 = K_2O + 2MnO + 5O \\
5SO_2 + 5O = 5SO_3 \\
5SO_3 + 5H_2O = 5H_2SO_4 \\
K_2O + H_2SO_4 = K_2SO_4 + H_2O \\
2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O \\
\hline
2K\overset{+7}{Mn}O_4 + 5\overset{+4}{S}O_2 + 2H_2O = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 2H_2\overset{+6}{S}O_4
\end{array}$$

(vi) When SO_2 is passed through an *orange solution* of *acidified potassium dichromate,* SO_2 reduces $K_2Cr_2O_7$ to green coloured *chromic salt,* itself being oxidised to H_2SO_4.

$$\begin{array}{c}
K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O \\
3SO_2 + 3O = 3SO_3 \\
3SO_3 + 3H_2O = 3H_2SO_4 \\
K_2O + H_2SO_4 = K_2SO_4 + H_2O \\
Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O \\
\hline
K_2\overset{+6}{Cr}_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + \overset{+3}{Cr}_2(SO_4)_3 + H_2O
\end{array}$$

Acidified $KMnO_4$ and $K_2Cr_2O_7$ solutions are reduced by both SO_2 and H_2S. Both the gases reduce $KMnO_4$ to manganous salt and as a result the pink colour of the solution becomes colourless, the *only difference* is that, in case of SO_2, $KMnO_4$ is reduced to give a clear colourless solution, but in case of H_2S a dirty colourless solution is obtained due to the precipitation of sulphur. Both SO_2 and H_2S reduce $K_2Cr_2O_7$ to chromic salt and as a result the orange colour of the solution turns green. The only difference is that, in case of SO_2 a clear green solution is obtained as SO_2 is oxidised to give H_2SO_4 but in case of H_2S a dirty green solution is obtained as H_2S is oxidised to sulphur and this free sulphur makes the solution turbid.

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S\downarrow$$

(vi) SO_2 reduces *nitric acid* to *nitrogen dioxide.*

$$\overset{+4}{S}O_2 + 2H\overset{+5}{N}O_3 = H_2\overset{+6}{S}O_4 + 2\overset{+4}{N}O_2$$

(vii) It also reduces *hydrogen peroxide* to water, itself being oxidised to SO_3 which ultimately converts to H_2SO_4 by reacting with H_2O.

$$H_2O_2 + SO_2 = H_2O + SO_3\ ; \qquad SO_3 + H_2O = H_2SO_4$$

(viii) It reduces *iodates* in aqueous solution to produce *free iodine* and thus the *clear solution turns brown.*

$$2K\overset{+5}{I}O_3 + 5\overset{+4}{S}O_2 + 4H_2O = I_2 + 3H_2\overset{+6}{S}O_4 + 2KHSO_4$$

5. **Oxidising property :** In some cases sulphur dioxide *acts as an oxidising agent.*

(i) *Burning magnesium, iron,* continue to burn in sulphur dioxide with the formation of the respective *oxides* and *sulphides.*

$$3\overset{0}{Fe} + SO_2 = 2\overset{+2}{Fe}O + FeS$$

(ii) The oxidising property of SO_2 is also exhibited when *burning sodium* or *potassium* is introduced in it.

$$4\overset{0}{Na} + 3SO_2 = Na_2SO_3 + \overset{+1}{Na_2}S_2O_3$$

(iii) When SO_2 is passed over *red hot coke* at 1100°C, carbon is oxidised to *carbon dioxide.*

$$SO_2 + \overset{0}{C} = \overset{+4}{C}O_2 + S$$

(iv) When SO_2 is passed through an *acidified solution of ferrous chloride,* ferrous chloride is oxidised to give a yellow solution of *ferric chloride.*

$$4FeCl_2 + 4HCl + SO_2 = 4FeCl_3 + 2H_2O + S \downarrow$$

(v) *Hydrogen sulphide* is oxidised by SO_2 to *sulphur* in the presence of *moisture.*

$$\overset{+4}{S}O_2 + 2H_2\overset{-2}{S} = 2H_2O + 3\overset{0}{S} \downarrow$$

This reaction proves that H_2S is stronger reducing agent than SO_2.

• SO_2 can act as a reducing agent as well as an oxidising agent— explain why.

$$\left[\ H_2\overset{-2}{S} \quad \overset{0}{S} \quad \overset{+4}{S}O_2 \quad H_2\overset{+6}{S}O_4\ \right]$$

In sulphur dioxide, the S atom is in +4 oxidation state. The next higher oxidation state of S-atom is +6 as in H_2SO_4 and the lower oxidation state of S atom is 0 as in free sulphur or −2 as in H_2S. Thus, the S atom of SO_2 has the scope to increase its oxidation number from (+4) to (+6) or to decrease its oxidation number from (+4) to (0) or (−2).

(i) Now when the S atom of SO_2 increases its oxidation number from (+4) to (+6) it is oxidised and this oxidation of S atom is brought out by reducing other substances. Under this condition SO_2 exhibits the reducing property e.g,. SO_2 reduces bromine to hydrobromic acid itself being oxidised to H_2SO_4.

reduced

$$\overset{+4}{S}O_2 + \overset{0}{Br_2} + 2H_2O = 2H\overset{-1}{Br} + H_2\overset{+6}{S}O_4$$

increase of O.N from (+4) to (+6)—oxidised

(ii) When the S-atom in SO_2 decreases its oxidation number from (+4) to (0) or (−2), it is reduced, and this reduction is brought out by oxidising the other substances.

Under this condition SO_2 exhibits the oxidation property e.g., sulphur dioxide oxidises H_2S to give a yellow precipitate of S, itself being reduced to sulphur.

$$\overset{\text{decrease of ON}-\text{reduced}}{\underbrace{2H_2\overset{-2}{S} + \overset{+4}{S}O_2 = 2H_2O + 3\overset{0}{S}}_{\text{oxidised}}}\downarrow$$

6. **Formation of additive compounds :** SO_2 forms additive compounds with some elements or compounds e.g., with chlorine in presence of sun light it forms *sulphuryl chloride.*

$$SO_2 + Cl_2 = SO_2Cl_2$$

$$Na_2O_2 + SO_2 = Na_2SO_4$$

Lead dioxide combines with SO_2 to form *lead sulphate.*

$$PbO_2 + SO_2 = PbSO_4$$

7. At *high temperature* (1200°C) SO_2 decomposes to produce *sulphur* and *sulphur trioxide.* In this reaction SO_2 is partly oxidised to SO_3 and partly reduced to free sulphur. It is therefore an example of disproportionation reactions

$$3\overset{+4}{S}O_2 = 2\overset{+6}{S}O_3 + \overset{0}{S}$$

8. **Bleaching property :** *Perfectly dry SO_2 has no bleaching property* but *in presence of moisture* it can bleach the vegetable colouring matters. It is probably due to the fact that in presence of moisture SO_2 at first reacts with water producing. H_2SO_4 with the evolution of nascent hydrogen. This nascent hydrogen bleaches the colouring matter to a colourless compound by reduction.

$$SO_2 + 2H_2O = H_2SO_4 + 2H$$

$$\text{Colouring matter} \xrightarrow[\text{reduction}]{[H]} \text{Reduced colourless product}$$

- **Comparison of the bleaching property of SO_2 and Cl_2 :**

(i) Both SO_2 and Cl_2 cannot bleach in dry state, but both of them can bleach the colouring matter in presence of moisture.

(ii) In presence of moisture SO_2 liberates nascent hydrogen and this nascent hydrogen bleaches the colouring matter to colourless product by reduction.

$$SO_2 + 2H_2O = H_2SO_4 + 2H$$

$$\text{Colouring matter} \xrightarrow[\text{reduction}]{[H]} \text{Reduced colourless product}$$

On the other hand chlorine, in presence of moisture evolves nascent oxygen which bleaches the cólouring matter to colourless product by oxidation.

$$Cl_2 + H_2O = 2HCl + O$$

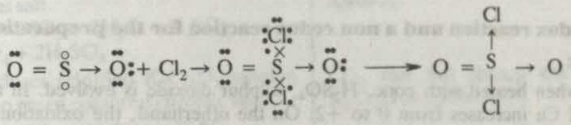
$$\text{Colouring matter} \xrightarrow[\text{oxidation}]{[O]} \text{Oxidised colourless product}$$

(iii) The bleaching action of SO_2 is not permanent. The original colour of the fabrics bleached by SO_2 may be restored when left exposed to air due to the oxidising action of oxygen of air. The bleaching action of Cl_2 is permanent. Once bleached by Cl_2, the substance cannot restore its original colour.

(iv) SO_2 is milder bleaching agent than Cl_2 and so delicate fabrics like silk, wool etc., are bleached by SO_2 as these delicate fabrics may be affected by the action of Cl_2.

- **SO_2 can form additive compounds but CO_2 cannot—explain why.**

In the molecule of SO_2, the S atom has a lone pair of electrons. These electrons can be donated to the monovalent atom like Cl to complete its octet. Thus two atoms of chlorine accepts one electron each from the lone pair of electrons of SO_2 to form sulphuryl chloride.



In the molecule of CO_2 the C atom has no such lone pair of electrons. Conse quently C atom has no scope to donate any electron to other atoms, and thus it cannot form additive compounds like SO_2.

- **Prove that sulphur di-oxide contains sulphur :**

Sulphur dioxide is dissolved in water and a saturated solution of SO_2 is produced. This saturated aqueous solution of SO_2 is taken in a sealed glass tube and is heated to 150°C for some time and then allowed to cool. A light yellow precipitate is found to form inside the tube. It is collected and washed well with water and dried. The solid thus obtained is soluble in CS_2 and burns in air producing a light blue flame with the evolution of a gas having a suffocating smell of burning sulphur. When this gas is passed through an acidified solution of $K_2Cr_2O_7$, the solution turns green from orange. This proves that the evolved gas is SO_2 and this SO_2 is formed by the burning of the yellow solid obtained from the aqueous solution of SO_2. Thus it is proved that the yellow solid is nothing but sulphur and this sulphur has come from SO_2.

$$H_2O + SO_2 = H_2SO_3$$
$$3H_2SO_3 = S\downarrow + 2H_2SO_4 + H_2O$$

- **Prove that SO_2 is a strong reducing agent :**

(i) An acidified solution of potassium permanganate is taken in a test tube and sulphur dioxide is passed through it. It is found that the pink colour of the solution is decolourised due to the formation of colourless manganous salt. Thus it is proved that SO_2 has reduced $KMnO_4$ to manganous salt.

$$2K\overset{+7}{Mn}O_4 + 5\,SO_2 + 2H_2O = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 2H_2SO_4$$

(ii) An acidified solution of potassium dichromate (orange) is taken in a test tube and SO_2 gas is bubbled through it. It is found that the orange colour of the solution turns green. This is due to the formation of green chromic salt. Thus, it is proved that SO_2 has reduced $K_2Cr_2O_7$ to chromic salt (green).

$$K_2\overset{+6}{Cr_2}O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + H_2O$$

(iii) Red coloured bromine water is taken in a test tube and SO_2 gas is passed through it. It is observed that the red colour of bromine water has become colourless. This is due to the formation of colourless HBr. Thus it is proved that SO_2 has reduced Br_2 to HBr.

$$SO_2 + \overset{0}{Br_2} + 2H_2O = 2H\overset{-1}{Br} + H_2SO_4$$

- **Prove that SO_2 can act as an oxidising agent :**

An acidified solution of ferrous chloride (colourless) is taken in a test tube and SO_2 gas is bubbled through it when the colourless solution turns yellow. This is due to the formation of ferric salt. Thus it is proved that SO_2 has oxidised ferrous chloride (colourless) solution to ferric chloride solution (yellow).

$$4\overset{+2}{Fe}Cl_2 + 4HCl + SO_2 = 4\overset{+3}{Fe}Cl_3 + S + 2H_2O$$

- **Illustrate a redox reaction and a non redox reaction for the preparation of SO_2.**

(i) **Redox reaction :**

Copper turnings when heated with conc. H_2SO_4, sulphur dioxide is evolved. In this reaction the oxidation number of Cu increases from 0 to +2. On the otherhand, the oxidation number of S is decreased from +6 to +4. Thus copper is oxidised to $CuSO_4$ and H_2SO_4 is reduced to SO_2. As oxidation and reduction have taken place simultaneously in this reaction—it is a redox reaction.

reduction

$$\overset{0}{Cu} + 2H_2\overset{+6}{S}O_4 = \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + 2H_2O$$

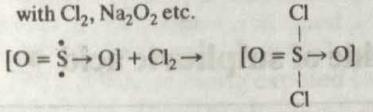
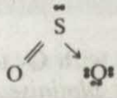
oxidation

(ii) Calcium sulphite on being treated with dilute HCl, $CaCl_2$ is produced with the liberation of SO_2. It is found that there is no change in the oxidation number of any atom involved in the reaction. So it is not a redox reaction.

$$Ca\overset{+4}{S}O_3 + 2H\overset{-1}{Cl} = Ca\overset{-1}{Cl_2} + \overset{+4}{S}O_2 + H_2O$$

- **Comparison of the properties of SO_2 and CO_2 :**

Sulphur dioxide (SO_2)	**Carbon dioxide (CO_2)**
(1) It is a colourless gas having a smell of burning sulphur.	A colourless and odourless gas.
(2) Heavier than air.	Heavier than air.
(3) Fairly soluble in water, can be liquefied to a colourless liquid by cooling in a freezing mixture.	It is fairly soluble in water and can be liquefied to a colourless liquid by applying pressure at ordinary temperature.
(4) It is neither combustible nor a supporter of combustion but burning Na, K, Mg, Fe etc., continue to burn in it. $3Fe + SO_2 = 2FeO + FeS$ $4Na + 3SO_2 = Na_2SO_3 + Na_2S_2O_3$	It is neither combustible nor a supporter of combustion but strongly heated metals like Na, K, Mg etc., continue to burn in it with the formation of oxides. $2Mg + CO_2 = 2MgO + C$
(5) An acidic oxide, forms sulphurous acid with water. $H_2O + SO_2 = H_2SO_3$	An acidic oxide—forms carbonic acid when it is dissolved in water. $CO_2 + H_2O = H_2CO_3$
(6) It reacts with alkalis to form sulphite and bisulphite salts. $SO_2 + 2NaOH = Na_2SO_3 + H_2O$ $Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3$	It reacts with alkalis to form carbonate and bicarbonate salts. $CO_2 + 2NaOH = Na_2CO_3 + H_2O$ $Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$
(7) When SO_2 is passed through lime water, the lime water turns milky due to the formation of sulphite. On passing excess of SO_2 the milkiness disappears due to the formation of soluble Ca bisulphite. $Ca(OH)_2 + SO_2 = CaSO_3 \downarrow + H_2O$ $CaSO_3 + SO_2 + H_2O = Ca(HSO_3)_2$	When CO_2 is passed through lime water, the lime water turns milky due to the formation of $CaCO_3$. On passing excess of CO_2 the milkiness disappears due to the formation of $Ca(HCO_3)_2$. $Ca(OH)_2 + CO_2 = CaCO_3 \downarrow + H_2O$ $CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$

Sulphur dioxide (SO_2)	**Carbon dioxide (CO_2)**
(8) SO_2 has got reducing property. It can reduce acidified $KMnO_4$ solution (pink) to colourless manganous salt. $2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$ It also reduces acidified $K_2Cr_2O_7$ solution (orange) to green coloured chromic salt. $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$	No such reduction can be brought out by CO_2. It can not decolourise the pink solution of $KMnO_4$. CO_2 can not change the orange colour of $K_2Cr_2O_7$ solution.
(9) SO_2 can act as an oxidising agent. It can oxidise ferrous chloride solution (colourless) to ferric chloride (yellow). Burning carbon is oxidised to CO_2. $4FeCl_2 + SO_2 + 4HCl = 4FeCl_3 + S + 2H_2O$ $C + SO_2 = CO_2 + S$	CO_2 can act as an oxidising agent. At high temperature CO_2 oxidises metallic zinc to give ZnO but it cannot oxidise $FeCl_2$ solution. $Zn + CO_2 = ZnO + CO \uparrow$
(10) SO_2 has bleaching property. It can bleach coloured matters by reduction.	CO_2 has no such bleaching property.
(11) Due to the presence of lone pair of electrons in S-atoms, it can form additive compounds with Cl_2, Na_2O_2 etc.  $[O = \overset{\cdot}{\underset{\cdot}{S}} \rightarrow O] + Cl_2 \rightarrow [O = \overset{Cl}{\underset{Cl}{S}} \rightarrow O]$	As the carbon atom in CO_2 has no loan pair of electrons, CO_2 cannot form additive compounds.
(12) SO_2 molecule has an angular structure ; the O—S—O bond angle being 120°. So it has dipole moment. 	CO_2 molecule has a linear structure the C atom being placed in the middle. It is a non polar molecule. $O = C = O$

• Tests of sulphur dioxide :

Sulphur dioxide may be identified by the following tests :—

(i) It is a colourless gas having a smell of *burning sulphur*.

(ii) A piece of blotting paper soaked in an acidified solution of $K_2Cr_2O_7$, on being introduced in a jar of SO_2, the *orange colour* of $K_2Cr_2O_7$ turns green due to the reduction of $K_2Cr_2O_7$ to *green chromic salt*.

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

(iii) The *pink colour* of the acidified solution of $KMnO_4$ is discharged when SO_2 is passed through it, as $KMnO_4$ is reduced by SO_2 to produce colourless manganous salt.

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(iv) A piece of blotting paper, soaked in KIO_3 and starch solution, is introduced in a jar of SO_2. The paper turns blue as KIO_3 is reduced by SO_2 to free iodine which turns starch blue.

$$2KIO_3 + 5SO_2 + 4H_2O = 3H_2SO_4 + 2KHSO_4 + I_2$$
$$I_2 + \text{starch} \rightarrow \text{turns blue.}$$

- **Uses of SO_2 :**

(i) SO_2 is chiefly used in the manufacture of H_2SO_4.

(ii) It is also used in the preparation of many useful salts like metallic sulphites and bisulphites. These are used in the paper industry, as bleaching agent and in photography.

(iii) SO_2 is used as a disinfactant and as a germ killer in agriculture.

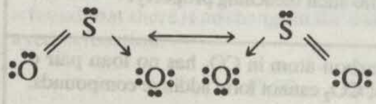
(iv) Liquid SO_2 is used as a refrigerating agent.

(v) It is used as antichlor to remove excess Cl_2 from materials bleached by Cl_2.

(vi) It is used in preserving fruits, meat, wine etc., and as a bleaching agent for bleaching silk, wool, straw etc.

- **Molecular structure of SO_2 :**

The molecule of SO_2 is 'V' shaped, the O—S—O bond angle being 120°. Due to this shape SO_2 is a dipolar molecule. One of the oxygen atom is connected to S-atom by covalent double bond and the other is joined by a co-ordinate bond. Due to the presence of lone pair of electrons in SO_2, it can *act as Lewise base*. The structure of SO_2 molecule is regarded as a resonance hybrid of the two structures shown in the side figure.



• Sulphur trioxide—anhydride of sulphuric acid •

Mol formula : SO_3 Mol wt : 80

6.11. Preparation of sulphur trioxide.

(i) By the direct combination of SO_2 and O_2.

[A] **Principle :** Oridinarily SO_2 cannot combine directly with O_2 to form SO_3. When a mixture of SO_2 and air or oxygen is passed over *platinised asbestos* or *vanadium pentoxide* heated to 450°C, SO_2 directly combines with O_2 and is oxidised to sulphur trioxide. The reaction is *reversible* and the *forward reaction is exothermic*.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + \text{heat}.$$

[B] **Procedure :** In the laboratory SO_3 is prepared by passing a mixture of SO_2 and O_2 through a combustion tube consisting of platinised asbestos. The catalyst is heated to about 450°C by a burner and the mixture of SO_2 and O_2 is passed over it, when SO_2 is oxidised by O_2 to produce white fumes of SO_3. This white vapour of SO_3 is

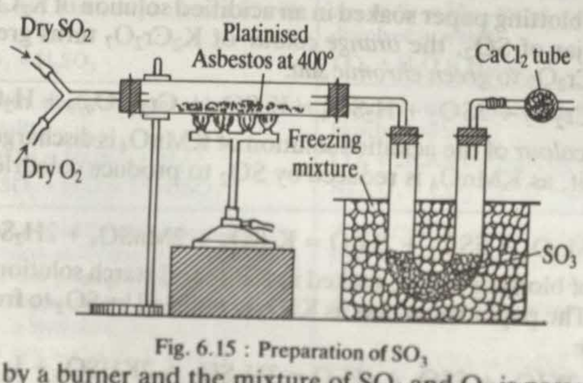


Fig. 6.15 : Preparation of SO_3

passed through a tube kept in a freezing mixture where SO_3 is collected as colourless transparent crystals. The atmospheric moisture is prevented from entering into the U-tube by fitting it with a guard tube containing fused $CaCl_2$.

(ii) By the dehydration of conc. H_2SO_4.

Sulphur trioxide may also be produced by distilling *conc. H_2SO_4* with *phosphorus pentoxide.* Conc. H_2SO_4 is dehydrated by P_2O_5 to produce SO_3 and *meta phosphoric acid.* The dense white vapours of SO_3 produced in the distilling flask are passed through a U-tube kept in a freezing mixture. SO_3 is collected in the U-tube as transparent colourless crystals.

$$H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$$

(iii) From metallic sulphates and sulphides, SO_3 is obtained by heating *ferric sulphate, ferrous sulphate* or *sodium bi sulphate.*

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3 \uparrow$$
$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$
$$2NaHSO_4 = Na_2SO_4 + SO_3 + H_2O$$

6.12. Properties of SO_3.

[A] **Physical :** (i) SO_3 is colourless transparent and crytalline solid. (ii) In solid state it exists in two forms—α SO_3 and β SO_3. α SO_3 is obtained as colourless needle shaped crystals, when anhydrous SO_3 vapours are cooled by liquid air. Its melting point is 17°C. α SO_3 on being exposed to moisture, changes to silky white, soft and asbestos like solid. This form in known as β SO_3. It sublimates at 50°C.

[B] **Chemical :**

(i) ***Action with water :*** SO_3 has a strong affinity for water. It reacts violently with water with a hissing sound producing *sulphuric acid* and *pyro-sulphurc acid* or *oleum.*

$$SO_3 + H_2O = H_2SO_4 \qquad H_2O + 2SO_3 = H_2S_2O_7$$

This reaction takes place with the evolution of much heat. When SO_3 is kept exposed in air, it combines with the moisture to form white fumes of H_2SO_4 particles.

- **Sulphur trioxide is called the anhydride of sulphuric acid—Explain why.**

Conc. H_2SO_4 on being treated with P_2O_5 is converted to sulphur trioxide.

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3$$

On the other hand, when water is added to SO_3, it is converted to H_2SO_4

$$H_2O + SO_3 = H_2SO_4$$

For this reason SO_3 is called the anhydride of H_2SO_4.

(ii) ***Action on basic oxides :*** SO_3 is an acidic oxide and so it reacts with many *basic oxides and alkalis* to produce *metallic sulphates.*

$$Na_2O + SO_3 = Na_2SO_4, \qquad BaO + SO_3 = BaSO_4$$
$$2NaOH + SO_3 = Na_2SO_4 + H_2O$$

(iv) ***Action with acids :***

(a) SO_3 combines with *hydrochloric acid* to form *chloro sulphonic acid.*

$$SO_3 + HCl = Cl\,SO_3\,H$$

(b) It is absorbed by *conc. H_2SO_4* to produce *Pyrosulphuric acid (oleum)* or *fuming sulphuric acid.*

$$H_2SO_4 + SO_3 = H_2S_2O_7$$

(iv) SO_3 decomposes to give *SO_2 and oxygen* when it is passed through a *red hot tube.*

$$2SO_3 = 2SO_2 + O_2$$

(v) ***Oxidising property :***

(a) Sulphur trioxide oxidises colourless *hydrobromic acid* to form red vapours of *bromine.*

$$2H\overset{-1}{Br} + \overset{+6}{S}O_3 = \overset{0}{Br_2} + \overset{+4}{S}O_2 + H_2O$$

(b) *Phosphorus pentachloride* ignites in contact with SO_3 with the liberation of *chlorine and phosphorus oxychloride.*

$$P\overset{-1}{Cl_5} + \overset{+6}{S}O_3 = POCl_3 + \overset{+4}{S}O_2 + \overset{0}{Cl_2}$$

(c) *Potassium iodide* is oxidised to give *free iodine.*

$$2K\overset{-1}{I} + 2\overset{+6}{S}O_3 = K_2SO_4 + \overset{+4}{S}O_2 + \overset{0}{I_2}$$

- **Conversion of SO_2 to SO_3 :**

(i) A mixture of SO_2 and O_2 is passed over *vanadium pentoxide* heated to 450°C when SO_2 is oxidised by O_2 to produce SO_3.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + \text{heat.}$$

(ii) **Conversion of SO_3 to SO_2 :**

(a) Sulphur trioxide on being passed through a red hot tube (1000°C) is decomposed to give SO_2 and O_2. The mixture is passed through NaOH solution when SO_2 reacts with NaOH to form Na_2SO_3 and oxygen passes out. SO_2 is obtained when Na_2SO_3 thus obtained is reacted with dil. HCl.

$$2SO_3 = 2SO_2 + O_2$$

$$SO_2 + 2NaOH = Na_2SO_3 + H_2O$$

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2\uparrow + H_2O$$

(b) SO_3 is absorbed by conc. H_2SO_4 to form oleum. A calculated amount of water is added to oleum when conc. H_2SO_4 is obtained. Conc. H_2SO_4 thus obtained on being heated with copper turnings yields SO_2.

$$SO_3 + H_2SO_4 = H_2S_2O_7\ ; \qquad H_2S_2O_7 + H_2O = 2H_2SO_4$$

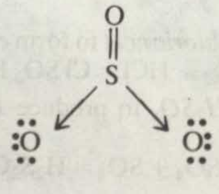
$$Cu + 2H_2SO_4 = CuSO_4 + SO_2\uparrow + 2H_2O$$

- **Uses of sulphur trioxide :**

It is used in the preparation of *sulphuric acid.* It is also used to produce ***oleum*** and *chloro sulphonic acid.*

- **Structure of sulphur trioxide.**

At an ordinary temperature SO_3 molecule has a planner triangular structure. The S—O bond distance is 1.43 Å. In SO_3 molecule one of the S—O bond is connected by a covalent double bond and the other two are joined by co-ordinate bonds. There is no lone pair of electrons in SO_3. Each of O—S—O bond angles is exactly 120°.



- **Comparison of the properties of SO_2 and SO_3 :**

Properties	Sulphur dioxide (SO_2)	Sulphur trioxide (SO_3)
(1) Physical state, colour and odour	A colourless gas having a suffocating smell of burning sulphur	A transparent and colourless crystalline solid.
(2) Solubility	Fairly soluble in water. The aqueous solution on heating evolves SO_2.	Very hygroscopic substance,—has a strong affinity for water. It dissolves in water evolving much heat.
(3) Acid property	An acidic oxide—dissolves in water producing unstable dibasic sulphurous acid which turns blue litmus red. $SO_2 + H_2O = H_2SO_3$	A strong acidic oxide—dissolves in water producing very stable dibasic sulphuric acid which turns blue litmus red. $SO_3 + H_2O = H_2SO_4$
(4) Formation of salts	It reacts with the basic oxide or alkali with the formation of two types of salt—bisulphite and sulphite. $NaOH + SO_2 = NaHSO_3$ $2NaOH + SO_2 = Na_2SO_3 + H_2O$	It reacts with the basic oxide or alkali with the formation of two types of salt—bisulphate and sulphate. $NaOH + SO_3 = NaHSO_4$ $2NaOH + SO_3 = Na_2SO_4 + H_2O$
(5) Reducing property	A strong reducing agent. It reduces acidified $KMnO_4$ solution to colourless manganous salt and $K_2Cr_2O_7$ solution to green chromic salt.	It has no reducing property.
(6) Oxidising property	It has oxidising property. It can oxidise H_2S to form yellow precipitate of sulphur. $SO_2 + 2H_2S = 2H_2O + 3S$	A strong oxidising agent—it can oxidise metals to produce sulphates. It oxidises colourless HBr to red coloured Br_2. $SO_3 + 2HBr = H_2O + Br_2 + SO_2$
(7) Bleaching property	A mild bleaching agent—bleaches the coloured matters by reduction	It has no bleaching property.

• OXYACIDS OF SULPHUR •

Sulphur forms a large number of oxyacids. According to the similarities in their structures these acids are classified as follows :

1. *Sulphoxylic acid :* H_2SO_2

2. *Sulphurous acid series :*

(i) Sulphurous acid (H_2SO_3), (ii) Hypo sulphurous acid ($H_2S_2O_4$), (iii) Thiosulphurous acid ($H_2S_2O_2$).

3. *Sulphuric acid series :*

(i) Sulphuric acid (H_2SO_4), (ii) Thio sulphuric acid ($H_2S_2O_3$), (iii) Pyro sulphuric acid ($H_2S_2O_7$).

4. *Thionic acid series :*
(i) Dithionic acid ($H_2S_2O_6$), (ii) Poly thionic acid ($H_2S_nO_6$) [$n = (3, 4, 5, 6)$].

5. *Peroxy persulphuric acid series :*
(i) Permono sulphuric acid (H_2SO_5) (*Caro's acid*), (ii) Perdisulphuric acid (*Marshall's acid*) ($H_2S_2O_8$).

Sulphurous acid (H_2SO_3)

6.13. Preparation of sulphurous acid.

(1) Sulphurous acid can be obtained by dissolving sulphur dioxide in water.

$$SO_2 + H_2O = H_2SO_3$$

Sulphurous acid is very unstable compound. It cannot be isolated in free state. It can be obtained only in dilute aqueous solution.

(2) Sulphurous acid may also be obtained by treating *sulphite* or *bisulphite* salts with *dilute HCl or H_2SO_4.*

$$Na_2SO_3 + 2HCl = 2NaCl + H_2SO_3$$
$$Ca(HSO_3)_2 + H_2SO_4 = CaSO_4 + 2H_2SO_3$$

(3) *Sulphurous acid from sulphuric acid.*

When *conc. H_2SO_4* is heated with *copper turnings, sulphur dioxide* is evolved. The evolved SO_2 is passed through water, when it is dissolved in water to form sulphurous acid.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$
$$H_2O + SO_2 = H_2SO_3$$

6.14. Properties of sulphurous acid.

(i) Sulphurous acid is colourless, unstable and weak acid. On being slightly heated, SO_2 is given off from the acid.

$$H_2SO_3 = H_2O + SO_2 \uparrow$$

(ii) *Acid property :*

Sulphurous acid is weak dibasic acid. It is ionised in water as

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \qquad HSO_3^- \rightleftharpoons H^+ + SO_3^=$$

Thus it forms two classes of salts — *acid sulphites or bisulphites* and *normal sulphites or sulphites.*

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O.$$
$$H_2SO_3 + 2NaOH = Na_2SO_3 + 2H_2O.$$

(iii) *Auto oxidation and reduction* (Disproportionation reaction) :

When sulphurous acid is heated in a sealed glass bulb to 150°C, a yellow precipitate of free sulphur separates out. In this reaction H_2SO_3 is partly oxidised to give *sulphuric acid* and is partly reduced to form free *sulphur*.

oxidised

$$3H_2\overset{+4}{S}O_3 = 2H_2\overset{+6}{S}O_4 + \overset{0}{S} + H_2O$$

reduced

(iv) *Reducing property :*

(a) It has a remarkable reducing property. When it is treated with *chlorine,* or *bromine water* or water containing suspended iodine, it reduces the halogens to form their respective hydracids and itself being oxidised to H_2SO_4.

$$\overset{0}{Cl_2} + H_2\overset{+4}{S}O_3 + H_2O = 2H\overset{-1}{Cl} + H_2\overset{+6}{S}O_4$$

$$\overset{0}{Br_2} + H_2\overset{+4}{S}O_3 + H_2O = 2H\overset{-1}{Br} + H_2\overset{+6}{S}O_4$$

(b) Yellow *ferric chloride* solution turns colourless when sulphurous acid is treated with it. Ferric chloride is reduced by H_2SO_3 to form *ferrous chloride.*

$$2\overset{+3}{Fe}Cl_3 + H_2SO_3 + H_2O = 2\overset{+2}{Fe}Cl_2 + H_2SO_4 + 2HCl$$

(c) H_2SO_3 can also decolourise an *acidified* $KMnO_4$ solution by reducing it to colourless *manganous salt.*

$$2K\overset{+7}{Mn}O_4 + 5H_2\overset{+4}{S}O_3 = K_2SO_4 + 2\overset{-2}{Mn}SO_4 + 2H_2\overset{+6}{S}O_4 + 3H_2O$$

(v) *Oxidising property :* H_2SO_3 exhibits oxidising property. It can oxidise *hydrogen sulphide* to free *sulphur.*

$$H_2\overset{+4}{S}O_3 + 2H_2\overset{-2}{S} = 3\overset{0}{S} + 3H_2O$$

- **Tests of sulphurous acid and sulphite salts :**

(i) Dry tests :

Sulphurous acid or sulphites are treated with dil. HCl or H_2SO_4 when SO_2 gas is evolved which has a suffocating smell of burning sulphur. When the evolved gas is passed through an acidified solution of $K_2Cr_2O_7$, the orange colour of the solution turns green due to the formation of chromic salt.

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O$$

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + \underset{\text{green}}{Cr_2(SO_4)_3} + H_2O$$

(ii) Wet tests :

When *barium chloride* solution is added to an aqueous solution of sulphite salt or sulphurous acid, a white precipitate of *barium sulphite* is obtained. The white precipitate is dissolved in dil. HCl when a clear solution is obtained. To this clear solution when bromine water is added and gently warmed, a white precipitate of barium sulphate is produced which is insoluble in HCl or HNO_3.

$$Na_2SO_3 + BaCl_2 = 2NaCl + BaSO_3 \downarrow$$

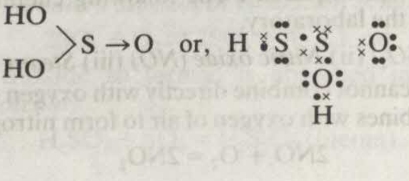
$$BaSO_3 + 2HCl = BaCl_2 + H_2SO_3$$

$$H_2SO_3 + Br_2 + H_2O = 2HBr + H_2SO_4$$

$$H_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2HCl$$

- **Uses of sulphurous acid :** It is used as a reducing agent and as a bleaching agent.

- **Structure of sulphurous acid :**



- **Sulphites :**

Sulphurous acid gives two classes of salts—*sulphites* and *bisulphites.*

Preparation of sulphites : (i) The sulphite salts are prepared by passing SO_2 into the solutions or suspensions of *metallic hydroxides* or *carbonates.*

$$2NaOH + SO_2 = Na_2SO_3 + H_2O$$

(ii) Sulphites are also formed by the reaction between *alkali metal sulphites* and *soluble salts of other metals.*

$$Na_2SO_3 + ZnSO_4 = ZnSO_3 \downarrow + Na_2SO_4$$

Properties of sulphites : (i) Sulphites of alkali metals and ammonium sulphite are soluble in water. The other normal sulphites are insoluble in water.

(ii) On being heated with dil. HCl or H_2SO_4 the sulphites are decomposed to give SO_2.

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2 \uparrow + H_2O$$

(iii) Sulphites on being *heated strongly* decompose *giving sulphates and sulphides.*

$$4CaSO_3 = CaS + 3CaSO_4$$

(iv) Sulphites are *oxidised to sulphates* in presence of *Cl_2 or Br_2 water.*

$$Na_2SO_3 + H_2O + Br_2 = Na_2SO_4 + 2HBr$$

(v) *Reducing property :* Sulphites possess reducing property. Thus (a) acidified $KMnO_4$ and $K_2Cr_2O_7$ solution are reduced to give manganous and chromic salts respectively.

$$K\overset{+7}{Mn}O_4 + 5Na_2SO_3 + 3H_2SO_4 = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 5Na_2SO_4 + 3H_2O$$

(b) *Halogens* are reduced to *hydracids.*

(c) *Iodic acid* is reduced to give *iodine.*

(d) An aqueous solution of a sulphite gives a white precipitate of $BaSO_3$ with $BaCl_2$ solution.

$$BaCl_2 + Na_2SO_3 = BaSO_3 \downarrow + 2NaCl$$

• Sulphuric acid or oil of vitriol •

Formula—H_2SO_4	**Molecular weight : 98**

This acid was prepared by the alchemists by distilling green vitriol ($FeSO_4, 7H_2O$) and absorbing the vapours in water. It was called *'Oil of vitriol'*. Because of its various applications in different industries, sulphuric acid is regarded as an important acid and may be called the *'King of chemicals'*.

6.15. Preparation of sulphuric acid.

Laboratory method :

[A] **Chemical ingradients required :** The following chemicals are required for preparation of H_2SO_4 in the laboratory.

(i) *Sulphur dioxide (SO_2)* (ii) *Nitric oxide (NO)* (iii) *Steam (H_2O)* (iv) *Air.*

[B] **Principle :** (i) SO_2 cannot combine directly with oxygen of air to form SO_3 but nitric oxide directly combines with oxygen of air to form nitrogen dioxide.

$$2NO + O_2 = 2NO_2$$

(ii) The nitrogen dioxide thus obtained is supposed to act as a catalyst in oxidising sulphur dioxide to sulphur trioxide when NO_2 is reduced to nitric oxide.

$$SO_2 + NO_2 = SO_3 + NO$$

Nitric oxide thus obtained is again oxidised by the oxygen of atmosphere which oxidises further amounts of SO_2 to SO_3. Thus nitric oxide acts as an *oxygen carrier.*

(iii) The SO_3 thus produced reacts with steam to form sulphuric acid.

$$H_2O + SO_3 = H_2SO_4$$

This mechanism of the formation of H_2SO_4 was suggested by *Berzelius.*

The second mechanism of the formation of H_2SO_4 *by this process was suggested by Lunge.*

(i) According to Lunge SO_2 and NO_2 combine with steam to produce an intermediate compound *nitrosi sulphuric acid* (H_2SO_4, NO).

$$2NO + O_2 = 2NO_2, \qquad SO_2 + NO_2 + H_2O = H_2SO_4, NO$$

(ii) In the second step the *nitrosi sulphuric acid* is oxidised by the oxygen of atmosphere to form *nitroso sulphuric* acid ($2HSO_4$, NO).

$$2H_2SO_4, NO + O = H_2O + 2HSO_4, NO$$

(iii) In the third step the *nitroso sulphuric acid* is decomposed by the steam to produce sulphuric acid.

$$2HSO_4, NO + H_2O = 2H_2SO_4 + N_2O_3$$
$$H_2O + 2SO_2 + N_2O_3 + O_2 = 2HSO_4, NO$$

• Preparation of H_2SO_4 from sulphur :

Sulphur is burnt in presence of air to produce sulphur dioxide. SO_2 thus formed is passed through water to produce H_2SO_3. Sulphurous acid is then oxidised by any oxidising agent (chlorine, nitric acid, hydrogen peroxide etc.) to yield sulphuric acid.

$$S + O_2 = SO_2 ; \qquad H_2O + SO_2 = H_2SO_3$$
$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$$
$$H_2SO_3 + Cl_2 + H_2O = 2HCl + H_2SO_4$$

6.16. Large scale preparation of sulphuric acid by contact process.

[A] **Theory of the process :**

(i) *Sulphur* or *iron pyrites* is burnt in presence of air to produce *sulphur dioxide.*

$$S + O_2 = SO_2 \uparrow$$
$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 \uparrow$$

(ii) In the second step, the produced sulphur dioxide is oxidised by the atmospheric oxygen to produce *sulphur trioxide.* This oxidation is carried out at 450°C by the catalytic action of *platinised asbestos* or *vanadium pentoxide.*

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45.2 \text{ k cal}$$

(iii) The sulphur trioxide so formed is absorbed in 98% H_2SO_4 to form *pyrosulphuric acid* or *oleum.*

$$H_2SO_4 + SO_3 = H_2S_2O_7 \text{ (oleum)}$$

(iv) The resulting oleum is added to a calculated amount of water when 98% or even 100% sulphuric acid is produced.

$$H_2S_2O_7 + H_2O = 2H_2SO_4$$

[B] **Physico-chemical principle involved.**

$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45.2$ k cal—this is the principal reaction of the contact process which represents the conversion of SO_2 to SO_3.

It is found that the reaction is (i) *reversible,* (ii) the forward reaction is *exothermic.* (iii) In the forward reaction there is a decrease in volume of the product. Consequently it is obvious that the yield of SO_3 will be regulated by Le Chatelier's principle in this process.

(1) ***Effect of temperature :***

In this reversible reaction as the forward reaction is exothermic, the reverse reaction must be endothermic.

(a) If the temperature is increased in this reaction, according to Le Chatelier's principle, the reaction will proceed in a direction where the excess heat will be absorbed. As the reverse reaction is endothermic, the increase of temperature will favour the reverse reaction and as a result the yield of SO_3 will be poor.

(b) If the temperature is decreased, then the reaction will proceed in a direction where the loss of heat is recovered. As the forward reaction is exothermic, low temperature will favour the forward reaction and as a result the yield of SO_3 increases. Though the lowering of temperature increases the yield of SO_3, it decreases the speed of reaction considerably. As a result it takes much time to obtain a satisfactory amount of SO_3. Time is an important factor in the commercial process, consequently it is essential to find out a suitable temperature at which the reaction proceeds at a fair speed yielding a satisfactory quantity of SO_3. The temperature thus selected is known as the optimum temperature. In this reaction the optimum temperature has been found to be 450°C. So the reaction is carried out at 450°C.

(2) ***Effects of pressure :***

According to Le Chatelier's principle if the pressure is increased on a system in equilibrium, the reaction will proceed in a direction where the excess pressure is released. Release of pressure means the decrease in volume. Since the reaction proceeds in the forward direction with decrease in volume (3 vols change to 2 vols), the increase of pressure will favour the forward reaction and as a result there is a possibility of higher yield of SO_3 at a high pressure. But as the yield of SO_3 is satisfactory when the reaction is carried out at the optimum temperature in presence of catalyst, no attempt is made to improve the yield further by increasing the pressure. The process is actually carried out at 1.5 atmospheres. High pressure may bring about a greater corrosion of chambers.

(3) ***Catalyst :***

To accelerate the speed of the reaction and to reach the equilibrium quickly, it is essential to use a catalyst. The activity of a solid catalyst is much enhanced if it is used in a finely divided state to provide a greater surface contact. The best results are obtained when *platinised asbestos* is used, but it is very costly and rapidly loses its activity due to poisoning by As_2O_3, sulphuric acid fog, dust etc., which are present in the gases from pyrites burner. Hence utmost care has to be taken for the purification of the reacting gases when platinum is used as catalyst. Now a days most of sulphuric acid plants use *vanadium pentoxide* as a catalyst which is almost as active as platinum but is cheaper and is not easily poisoned.

(4) ***Effect of concentration of reactants and continuous removal of the produced SO_3.***

The equilibrium constant K_c of the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is given below—

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 \times [O_2]}$$

As the value of K_c at a fixed temperature is constant, it is obvious that the use of excess O_2 (air) will favour the forward reaction yielding more SO_3. The presence of O_2 in excess will increase the denominator in the above expression. Hence inorder to maintain the value of K_c, the numerator i.e., the concentration of SO_3 increases. So the concentration of O_2 is increased by using slight excess of air. Best results are obtained when O_2 and SO_2 are present in the molecular proportion of 3 : 2.

Again according to Chatelier's principle, the decrease of the concentration of SO_3 will favour the forward reaction. Consequently to make the reaction proceed in the forward direction, the SO_3 produced is continuously removed from the system.

(5) The gas mixture consisting of SO_2 and air must be completely freed from dust particles, sulphur, arsenious oxide, etc. These impurities, specially As_2O_3, poison the catalyst and the reaction is ultimately stopped.

[C] **Description of the process :**

(i) ***Production of sulphur dioxide.***

The sulphur dioxide is produced by burning sulphur or iron pyrites with excess air in *pyrites-burners*.

(ii) ***Purification of the gas mixture.***

The gas mixture from the pyrites-burners containing 8% SO_2, 10% O_2 and the rest N_2 is not pure. It contains impurities like As_2O_3, sulphur dust, sulphuric acid fog which act as poisons on the catalytic surface.

(a) The gas mixture is carefully purified by passing the gas, at first through a dust chamber, where the dust particles, sulphur, arsenious oxide and other suspended materials are made to settle down.

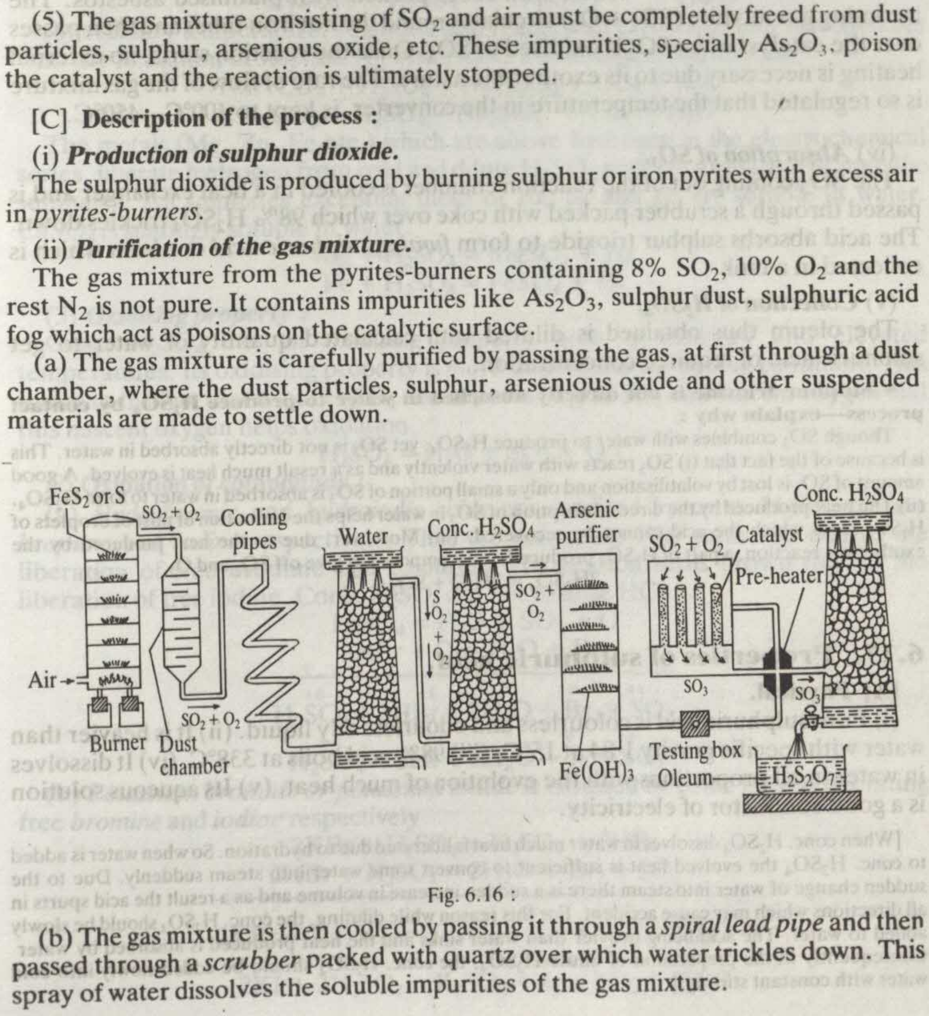


Fig. 6.16 :

(b) The gas mixture is then cooled by passing it through a *spiral lead pipe* and then passed through a *scrubber* packed with quartz over which water trickles down. This spray of water dissolves the soluble impurities of the gas mixture.

(c) The issuing gas mixture is then passed through a *drying tower* which is packed with coke and over which a stream of conc. H_2SO_4 trickles down. Here the gas mixture becomes completely freed from moisture.

(d) It is then passed through an *arsenic purifier* which contains precipitated $Fe(OH)_3$ kept on shelves. $Fe(OH)_3$ absorbs any As_2O_3 present in the gas mixture. The pure and dry gas mixture coming out of this purifier appears to be transparent.

(e) Before sending the gas mixture in the reaction chamber, its purity is tested by passing it through a *testing box*. Here the gas mixture is examined against a strong beam of light. The pure and dry gas mixture would appear transparent while passing through this box. If any particles of dust, or As_2O_3 are present in the gas mixture, they are illuminated due to tyndal effect.

(iii) ***Catalytic oxidation of SO_2 :*** The purified gas mixture is then led into a preheater where it is preheated to 400°—450°C by the hot gases coming out from the converter and is finally passed into catalyst chamber called converter. It is an iron chamber containing few verticle iron tubes packed with platinised asbestos. The incoming gas mixture ($SO_2 + O_2$) circulates round the hot iron tubes and then passes over the catalyst when SO_2 is oxidised to SO_3. Once the reaction starts, no external heating is necessary due to its exothermic nature. The rate of flow of the gas mixture is so regulated that the temperature in the converter is kept to 400°C—450°C.

(iv) ***Absorption of SO_3.***

The SO_3 coming out of the reaction chamber is cooled in a heat exchanger and is passed through a scrubber packed with coke over which 98% H_2SO_4 trickles down. The acid absorbs sulphur trioxide to form *fuming sulphuric acid* or *oleum* which is collected in a tank.

(v) ***Collection of H_2SO_4.***

The oleum thus obtained is diluted with calculated quantity of water to get sulphuric acid of required concentration.

- **Sulphur trioxide is not directly absorbed in water to produce H_2SO_4 by contact process—explain why :**

Though SO_3 combines with water to produce H_2SO_4, yet SO_3 is not directly absorbed in water. This is because of the fact that (i) SO_3 reacts with water violently and as a result much heat is evolved. A good amount of SO_3 is lost by volatilisation and only a small portion of SO_3 is absorbed in water to form H_2SO_4. (ii) The heat produced by the direct absorption of SO_3 in water helps the formation of mist of droplets of H_2SO_4 from which the acid cannot be recovered. (iii) Moreover, due to the heat produced by the exothermic reaction, a part of H_2SO_4 produced, is decomposed to give off SO_2 and O_2.

$$2H_2SO_4 = 2H_2O + SO_2 + O_2$$

6.17. Properties of sulphuric acid.

[A] Physical.

(i) Pure sulphuric acid is colourless and odourless oily liquid. (ii) It is heavier than water with specific gravity 1·84 at 15°C. (iii) 98% acid boils at 338°C. (iv) It dissolves in water in all proportions with the evolution of much heat. (v) Its aqueous solution is a good conductor of electricity.

[When conc. H_2SO_4 dissolves in water much heat is liberated due to hydration. So when water is added to conc. H_2SO_4 the evolved heat is sufficient to convert some water into steam suddenly. Due to the sudden change of water into steam there is a sudden increase in volume and as a result the acid spurts in all directions which may cause accident. For this reason while diluting, the conc. H_2SO_4 should be slowly added to water. The acid being heavier than water sinks and the heat produced is absorbed by water Consequently in the preparation of dilute H_2SO_4, the conc. H_2SO_4 should be added slowly into cold water with constant stirring.]

[B] Chemical :

(1) ***Effect of heat :*** When sulphuric acid is added dropwise or red hot pumice stones or when H_2SO_4 vapour is passed through red hot silica tube, sulphuric acid decomposes to form SO_2 and O_2.

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$

(2) ***Acid property :*** Sulphuric acid is a strong dibasic acid. In its aqueous solution it is completely ionised. Its ionisation takes place in two steps.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad H_2SO_4 \rightleftharpoons 2H^+ + SO_4^=$$

Its aqueous solution turns blue litmus red and reacts *with bases and alkalis to produce salts and water*. It has two replaceable hydrogen atoms and so it forms two series of salts—normal salt (sulphates) and acid salts (bisulphates).

$$\begin{array}{llll} MgO & + H_2SO_4 & = MgSO_4 & + H_2O \\ CaO & + 2H_2SO_4 & = Ca(HSO_4)_2 & + H_2O \\ NaOH & + H_2SO_4 & = NaHSO_4 & + H_2O \\ 2NaOH & + H_2SO_4 & = Na_2SO_4 & + 2H_2O \end{array}$$

At ordinary temperature, sulphuric acid reacts *with carbonates and bicarbonates* with the formation of *sulphates* or *bisulphates* liberating *carbon dioxide*.

$$NaHCO_3 + H_2SO_4 = NaHSO_4 + CO_2 + H_2O$$
$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$$

The metals (Mg, Zn, Fe etc.) which are above hydrogen in the electrochemical series, liberate hydrogen from cold and dilute H_2SO_4 with the formation of metallic sulphates. All sulphates excepting those of Ba, Sr and Pb are soluble in water. $CaSO_4$ is sparingly soluble in water.

$$Mg + H_2SO_4 = MgSO_4 + H_2$$
$$Fe + H_2SO_4 = FeSO_4 + H_2$$

(3) ***Oxidising property :***

Conc. H_2SO_4 has an oxidising property both at ordinary and elevated temperatures. Its oxidising property is *more exhibited at the boiling condition*. This is due to the fact that conc. H_2SO_4 decomposes to give SO_2 and *nascent oxygen* and this nascent oxygen helps oxidation.

$$H_2SO_4 = H_2O + SO_2 + O\uparrow$$

(i) Oxidation of compounds :

(a) *Hydrobromic* and *hydroiodic acids* are oxidised by conc. H_2SO_4 to free *bromine* and *iodine* respectively. Thus the colourless HBr turns red due to the liberation of free bromine and colourless HI solution turns brown due to the liberation of free iodine. Conc. H_2SO_4 can not oxidise HCl.

$$\begin{array}{c} H_2SO_4 = H_2O + SO_2 + O \\ 2HBr + O = H_2O + Br_2 \\ \hline H_2\overset{+6}{S}O_4 + 2H\overset{-1}{Br} = 2H_2O + \overset{0}{Br_2} + \overset{+4}{S}O_2 \end{array}$$

$$H_2\overset{+6}{S}O_4 + 2H\overset{-1}{I} = 2H_2O + \overset{0}{I_2} + \overset{+4}{S}O_2$$

(b) *Potassium bromide or potassium iodide* is oxidised by conc. H_2SO_4 liberating free *bromine* and *iodine* respectively.

$$\begin{array}{c} 2KBr + H_2SO_4 = K_2SO_4 + 2HBr \\ 2HBr + H_2SO_4 = 2H_2O + Br_2 + SO_2 \\ \hline 2K\overset{-1}{Br} + 2H_2\overset{+6}{S}O_4 = K_2SO_4 + \overset{0}{Br_2} + \overset{+4}{S}O_2 + 2H_2O \end{array}$$

$$2K\overset{-1}{I} + 2H_2\overset{+6}{S}O_4 = K_2SO_4 + \overset{0}{I_2} + \overset{+4}{S}O_2 + 2H_2O$$

(c) *Acidified ferrous salts* are oxidised by conc. H_2SO_4 to ferric salts e.g., colourless *ferrous sulphate* solution is oxidised to yellow *ferric sulphate.*

$$\begin{array}{c} H_2SO_4 = H_2O + SO_2 + O \\ 2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O \\ \hline 2\overset{+2}{Fe}SO_4 + 2H_2\overset{+6}{S}O_4 = \overset{+3}{Fe_2}(SO_4)_3 + 2H_2O + \overset{+4}{S}O_2 \end{array}$$

Acidified ferrous chloride is oxidised to *ferric chloride.*

$$\begin{array}{c} H_2SO_4 = H_2O + SO_2 + O \\ 2FeCl_2 + 2HCl + O = 2FeCl_3 + H_2O \\ \hline 2\overset{+2}{Fe}Cl_2 + 2HCl + H_2\overset{+6}{S}O_4 = 2\overset{+3}{Fe}Cl_3 + \overset{+4}{S}O_2 + 2H_2O \end{array}$$

(d) *Hydrogen sulphide* is oxidised to give a yellow precipitate of *free sulphur.*

$$\begin{array}{c} H_2SO_4 = H_2O + SO_2 + O \\ H_2S + O = H_2O + S \\ \hline H_2\overset{+6}{S}O_4 + H_2\overset{-2}{S} = \overset{0}{S} + \overset{+4}{S}O_2 + 2H_2O \end{array}$$

(ii) Oxidation of non metals :

(a) Burning *carbon* is oxidised by conc. H_2SO_4 to *carbon dioxide.*

$$\begin{array}{c} 2H_2SO_4 = 2H_2O + 2SO_2 + O_2 \\ C + O_2 = CO_2 \\ \hline 2H_2\overset{+6}{S}O_4 + \overset{0}{C} = \overset{+4}{C}O_2 + 2\overset{+4}{S}O_2 + 2H_2O \end{array}$$

(b) *Sulphur* on being treated with *hot* and *conc.* H_2SO_4, is oxidised to *sulphur dioxide.*

$$\begin{array}{c} (H_2SO_4 = H_2O + SO_2 + O) \times 2 \\ S + 2O = SO_2 \\ \hline 2H_2\overset{+6}{S}O_4 + \overset{0}{S} = 2H_2O + 3\overset{+4}{S}O_2 \end{array}$$

(c) *Phosphorus* is oxidised to *orthophosphoric acid* when it is treated with hot and conc. H_2SO_4.

$$\begin{array}{c} (H_2SO_4 = H_2O + SO_2 + O) \times 5 \\ 2P + 5O = P_2O_5 \\ P_2O_5 + 3H_2O = 2H_3PO_4 \\ \hline 5H_2\overset{+6}{S}O_4 + 2\overset{0}{P} = 2H_3\overset{+5}{P}O_4 + 5\overset{+4}{S}O_2 + 2H_2O \end{array}$$

(iii) Oxidation of metals :

Hot and *conc.* H_2SO_4 oxidises many metals, e.g., Cu, Zn, Ag, Mg, Al etc., to the corresponding *sulphates,* itself being reduced to SO_2.

$$\begin{array}{c} H_2SO_4 = H_2O + SO_2 + O \\ Cu + O = CuO \\ CuO + H_2SO_4 = CuSO_4 + H_2O \\ \hline \overset{0}{Cu} + 2H_2\overset{+6}{S}O_4 = \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + 2H_2O \end{array}$$

$$\begin{array}{llllll} \text{Similarly,} & Hg & + 2H_2SO_4 & = HgSO_4 & + SO_2 & + 2H_2O \\ & 2Ag & + 2H_2SO_4 & = Ag_2SO_4 & + SO_2 & + 2H_2O \\ & 2Al & + 6H_2SO_4 & = Al_2(SO_4)_3 & + 3SO_2 & + 6H_2O \\ & Zn & + 2H_2SO_4 & = ZnSO_4 & + SO_2 & + 2H_2O \end{array}$$

- **Conc. H_2SO_4 can oxidise but cannot reduce—explain why.**

The oxidation number of S atom in H_2SO_4 is (+6). This is the highest oxidation number of sulphur in its compounds. The next lower oxidation number of sulphur is (+4). So the S atom of H_2SO_4 has no scope to increase its oxidation number any further i.e., it cannot be oxidised. This is why H_2SO_4 does not behave as a reducing agent. On the other hand, the S atom in H_2SO_4 has the scope to decrease its oxidation number from (+6) to (+4) or (0) and thus it is reduced. This reduction of S atom in H_2SO_4 can only be brought out by oxidising the other substances. So H_2SO_4 cannot behave as a reductant but can act as oxidant.

(4) ***Strong affinity for water :***

Pure sulphuric acid has a strong affinity for water. Due to this property conc. H_2SO_4 is used as a *dehydrating agent* and is used for drying moist air or gases.

Conc. H_2SO_4 forms hydrates with a small amount of water having the composition (H_2SO_4, H_2O), (H_2SO_4, $2H_2O$), (H_2SO_4, $4H_2O$) etc. These hydrates can be isolated as colourless crystals at low temperatures.

Its affinity for water is so strong that it can absorb elements of water (*water of constitution*) from many organic compounds.

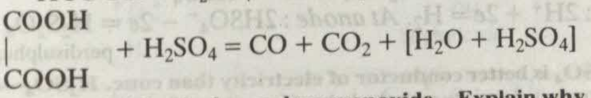
(a) Thus conc. H_2SO_4 on being added to sugar, the sugar becomes charred, as conc. H_2SO_4 abstracts the elements of water from sugar molecule ($C_{12}H_{22}O_{11}$) leaving black carbon as the residue.

$$C_{12}H_{22}O_{11} + [H_2SO_4] \rightarrow 12\,C + 11H_2O + [H_2SO_4]$$

It also *chars paper* which is composed of cellulose by removing water molecules from it.

(b) *Formic acid and oxalic acid* on being heated with conc. H_2SO_4, elements of water are absorbed from them and *carbon monoxide is given off.*

$$HCOOH + H_2SO_4 = CO + [H_2O + H_2SO_4]$$



$$\begin{array}{l}COOH\\ |\\ COOH\end{array} + H_2SO_4 = CO + CO_2 + [H_2O + H_2SO_4]$$

- **Conc. H_2SO_4 is not used for drying carbon monoxide—Explain why.**

Carbon monoxide is a reductant . On the other hand conc. H_2SO_4 is a strong oxidant. It is decomposed to give off nascent oxygen which can easily oxidises CO to form CO_2 Conc. H_2SO_4 being reduced to SO_2. Hence conc. H_2SO_4 is not suitable for drying CO.

$$\begin{array}{c}H_2SO_4 = H_2O + SO_2 + O\\ CO + O = CO_2\\ \hline H_2SO_4 + CO = CO_2 + SO_2 + H_2O\end{array}$$

(c) Conc. H_2SO_4 absorbs *water of crystallisation* from blue coloured copper sulphate crystals and converts it into white powder of anhydrous copper sulphate.

$$\underset{\text{blue crystal}}{CuSO_4, 5H_2O} + H_2SO_4 \rightarrow \underset{\text{white powder}}{CuSO_4} + [5H_2O + H_2SO_4]$$

[*The use of conc. H_2SO_4 for drying moist gases :*

Gases which do not react with conc. H_2SO_4 e.g., *oxygen, hydrogen, nitrogen, chlorine, carbon dioxide* etc., can be dried by conc. H_2SO_4.

Conc. H_2SO_4 can never be used for drying NH_3, H_2S, HBr, HI, CO etc., as conc. H_2SO_4 reacts with ammonia forming ammonium sulphate.

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

H_2S, HBr, HI are oxidised by conc. H_2SO_4 to produce S, Br_2 and I_2 respectively.

$$H_2S + H_2SO_4 = S + SO_2 + 2H_2O$$
$$2HX + H_2SO_4 = X_2 + SO_2 + 2H_2O \quad [X = Br_2, I_2]$$

(5) ***Displacement of volatile acids from their salts.***

Conc. H_2SO_4 is much less volatile (b.p. 338°C) than *nitric acid* or *hydrochloric acid.*

It can therefore displace nitric acid vapours from nitrates and hydrochloric acid vapours from chloride salts at high temperature.

$$NaCl + H_2SO_4 \xrightarrow{150°C} NaHSO_4 + HCl\uparrow$$

$$NaNO_3 + H_2SO_4 \xrightarrow{200°C} NaHSO_4 + HNO_3\uparrow$$

On the otherhand when any *metallic sulphate* is heated with *nitric acid* or *hydrochloric acid,* both being much volatile than H_2SO_4, volatilise out before H_2SO_4 is liberated.

(6) ***Formations of sulphonic acid.***

Conc. H_2SO_4 can introduce sulphonate radical into many organic compounds. Thus it reacts with *benzene* to form *benzene sulphonic acid.*

$$C_6H_6 + OH.SO_3H \rightarrow \underset{\text{benzene sulphonic acid}}{C_6H_5SO_3H} + H_2O$$

(7) ***Action on*** PCl_5 **:**

Phosphorus pentachloride reacts with conc. H_2SO_4 to form *chloro sulphonic acid* and *sulphuryl chloride.*

$$SO_2(OH)_2 + PCl_5 = \underset{\text{chloro sulphonic acid}}{SO_2(OH)Cl} + HCl + POCl_3$$

(8) In dilute solution H_2SO_4 ionises as $2H^+$ and $SO_4^=$ but conc. H_2SO_4 ionises as H^+ and HSO_4^-, consequently conc. H_2SO_4, on electrolysis perdisulphuric acid is liberated at the anode.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

At cathode : $2H^+ + 2e = H_2$. *At anode* : $2HSO_4^- - 2e = \underset{\text{perdisulphuric acid}}{H_2S_2O_8}$

- **Dilute H_2SO_4 is better conductor of electricity than conc. H_2SO_4—explain why.**

Electrolytes conduct electricity with the help of ions. According to Arrhenius theory of electrolytic dissociation, the degree of dissociation of an electrolyte increases with the dilution. Consequently the more the H_2SO_4 diluted, the more its molecules are dissociated to form more H^+ and $SO_4^=$ ions. But the molecules of conc. H_2SO_4 ionises much less in number than dilute H_2SO_4. Because of the greater number of ions in dil. H_2SO_4 solution, it is a better conductor of electricity than conc. H_2SO_4.

- **Sulphates :** Salts of sulphuric acid are known as sulphates. Sulphate salts are generally prepared *by the action of dilute sulphuric acid on metals, metallic oxides, hydroxides or carbonates.*

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
$$MgO + H_2SO_4 = MgSO_4 + H_2O$$
$$CuCO_3 + H_2SO_4 = CuSO_4 + CO_2 + H_2O$$
$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O$$

Insoluble sulphates are prepared by the action of soluble sulphates like Na_2SO_4 on soluble salts of Ba, Sr, Ca, Pb etc. $CaSO_4$ is sparingly soluble in water.

$$BaCl_2 + Na_2SO_4 = BaSO_4\downarrow + 2NaCl$$
$$Pb(NO_3)_2 + Na_2SO_4 = PbSO_4.\downarrow + 2NaNO_3$$

- **Properties of sulphates :**

(i) **Solubility :** With the exception of the sulphates of Ca, Ba, Sr, and Pb, most of the other metallic sulphates are soluble in water.

(ii) **Action of heat :** On strong heating sulphates are decomposed to give SO_2, where as $FeSO_4$ gives fumes of SO_3.

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$$

(iii) **Reduction :** On being *heated strongly with carbon*, the sulphates are reduced to *sulphides*.

$$BaSO_4 + 4C = BaS + 4CO$$
$$Na_2SO_4 + 4C = Na_2S + 4CO$$

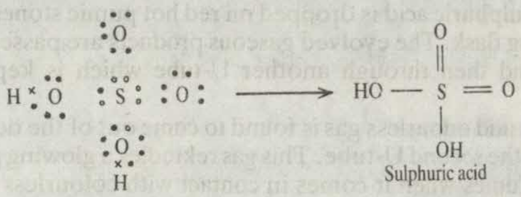
(iv) Aqueous solutions of sulphates give a *white precipitate of barium sulphate* on being treated with *barium chloride* solution. This white precipitate is insoluble in HCl or HNO_3.

$$K_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2KCl$$

(v) Many sulphates have the property of forming double sulphates like *Mohr's salt* $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$. The sulphates of trivalent metals have the property of forming double salts with those of alkali matals. Such salts are known as *alums* e.g., *potash atom* K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$.

- **Structure of H_2SO_4 and sulphate ions :**

In the molecule of sulphuric acid the two OH groups are directly attached to the sulphur atom and the two oxygen atoms are directly joined to the sulphur atom by double bond. Sulphuric acid may thus be represented as below.


Sulphuric acid

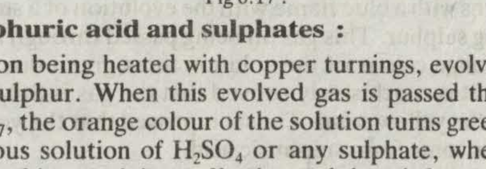

Sulphate ion

Fig 6.17 :

- **Tests of sulphuric acid and sulphates :**

(i) Conc H_2SO_4 on being heated with copper turnings, evolves SO_2 which has a smell of burning sulphur. When this evolved gas is passed through an acidified solution of $K_2Cr_2O_7$, the orange colour of the solution turns green.

(ii) To an aqueous solution of H_2SO_4 or any sulphate, when barium chloride solution is added, a white precipitate of barium sulphate is formed which is insoluble in HCl or HNO_3.

$$H_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2HCl$$
$$Na_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2NaCl$$

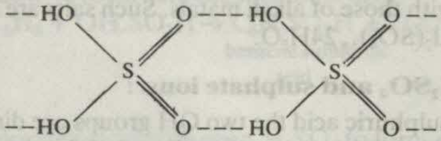
(iii) To identify the insoluble sulphate, the given sample is at first fused with excess of sodium carbonate and the product is extracted with distilled water. The filtrate is acidified with dil HCl and then treated with barium chloride solution when a white precipitate of barium sulphate is obtained which is insoluble in HNO_3.

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3 \downarrow$$
$$Na_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2NaCl$$

- **Uses of sulphuric acid :**

Sulphuric acid is largely used in various chemical industries and so it is known as *'The king of chemicals'*. It is used —(i) in the preparation of fertiliser's such as ammonium sulphate, super phosphate of lime etc., (ii) in the manufacture of many acids like nitric acid, hydrochloric acid, (iii) in the manufacture of paints and pigments, dyes and explosives, (iv) in refining petrolium and in filling storage cells, (v) in drying gases and for nitration and sulphonation of organic compounds, (vi) as an oxidising agent in the laboratory.

- The high boiling point (388°C), low volatility and viscous nature of concentrated H_2SO_4 are due to hydrogen bonding, for which a number of H_2SO_4 molecules are associated to form polymeric molecules.



- **Prove that sulphuric acid contains sulphur, oxygen and hydrogen :**

Concentrated sulphuric acid is dropped on red hot pumic stones taken in a round bottomed distilling flask. The evolved gaseous products are passed through a water cooled U-tube and then through another U-tube which is kept immersed in a freezing mixture.

(i) A colourless and odourless gas is found to come out of the delivery tube which is connected with the second U-tube. This gas rekindles a glowing piece of wood and produces brown fumes when it comes in contact with colourless nitric oxide. This gas is completely absorbed by alkaline pyrogallate solution. Thus it is proved that the gas coming out of the delivery tube is oxygen and this oxygen has come from sulphuric acid.

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2 \uparrow$$

(ii) The liquid obtained in the second U-tube is taken in a sealed tube and is heated to 150°C when a light yellow solid separates out. It is collected and washed well with distilled water. This yellow solid is found to be dissolved in CS_2. When ignited in air, it burns with a blue flame with the evolution of a suffocating gas having the smell of burning sulphur. This gas on being passed through an acidified solution of $K_2Cr_2O_7$, the orange colour of the solution turns green due to the formation of chromic salt. Thus it is conclusively proved that the gas is SO_2 which is formed by the combustion of the yellow solid. Thus it is proved that the yellow solid is sulphur and this sulphur has come from sulphuric acid.

(iv) The colourless liquid which deposits in the first U-tube turns white anhydrous copper sulphate blue. Thus it is proved that the colourless liquid is water. Now water contains hydrogen and this hydrogen has come from sulphuric acid.

- **Prove that sulphuric acid is an oxidising agent :**

(i) Conc. H_2SO_4 is added to colourless hydrobromic acid and the mixture is heated when red vapours of bromine are found to evolve. This proves that colourless HBr is oxidised by conc. H_2SO_4 to give free bromine.

$$2HBr + H_2SO_4 = Br_2 \uparrow + SO_2 + 2H_2O$$

(ii) A mixture of powdered charcoal and conc. H_2SO_4 is taken in a distilling flask and is heated. Reaction takes place with the evolution of a colourless gas mixture.

The gas mixture is passed in succession through two wash bottles—the first one containing acidified $K_2Cr_2O_7$ solution and the second one containing lime water. It is found that the orange solution of $K_2Cr_2O_7$ turns green and the clear solution of lime water turns milky. This proves that conc. H_2SO_4 has oxidised charcoal to produce CO_2, itself being reduced to SO_2. This SO_2 has turned acidified $K_2Cr_2O_7$ solution green due to the formation of chromic salt and CO_2 being unreacted with $K_2Cr_2O_7$ passes out and enters the second wash bottle and turns the lime water milky.

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$$

- **Prove that conc. H_2SO_4 is a strong dehydrating agent.**

A small amount of white crystals of cane sugar is taken in a watch glass and few drops of conc. H_2SO_4 are added to it. The white crystals of sugar turn black. Water is added to the residue and the black residue is separated by filtration. It is dried and is burnt in air when a colourless and odourless gas is evolved. The evolved gas turns lime water milky but cannot turn acidified $K_2Cr_2O_7$ solution green. Thus it is proved that the gas is CO_2 which is produced by the burning of the black residue in air. Thus it is proved that the black residue is carbon which is left behind when conc. H_2SO_4 has abstracted elements of water from sugar molecules.

$$C_{12}H_{22}O_{11} + [H_2SO_4] \rightarrow 12C + [11H_2O + H_2SO_4]$$

- **Difference in the properties of conc. H_2SO_4 and dil. H_2SO_4 :**

Properties	Conc. H_2SO_4	Dil. H_2SO_4
(1) Acid property	Less ionised and so less number of H^+ ions are produced. Consequently conc. H_2SO_4 is less strong acid than dil. H_2SO_4.	Most of the molecules are ionised, the degree of ionisation increases with the increase of dilution. So greater number of H^+ ions are produced. Consequently dil. H_2SO_4 is much stronger acid than conc. H_2SO_4.
(2) Affinity for water	Has a strong affinity for water. It can abstract the elements of water from many organic compounds leaving behind a precipitate of black carbon. It can absorb water of crystallisation from a hydrated salt.	Has no affinity for water. It cannot absorb water from blue vitriol nor can abstract elements of water from organic compounds.
(3) Action on metals	Oxidises different metals when heated to form sulphates, itself being reduced to SO_2	The replaceable H atoms are replaced by metals which are above H_2 in the electrochemical series.
(4) Action on non metal	Oxidises non metals like carbon, sulphur etc., to produce their oxides. $C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$	Has no action on non metals like C. S. P. etc.
(5) Electrolysis	Conc. H_2SO_4 (60%) on electrolysis liberates perdisulphuric acid at the anode. $H_2SO_4 \rightleftharpoons HSO_4^- + H^+$ Anode : $2HSO_4^- - 2e = H_2S_2O_8$	Hydrogen gas is liberated at the cathode and O_2 is liberated at the anode when dilute H_2SO_4 is electrolysed. $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^=$ $H_2O = 2H^+ + 2OH^-$ Cathode : $2H^+ + 2e = H_2$ Anode : $2OH^- - 2e = 2OH$ $4OH = 2H_2O + O_2$
(6) Action HBr and HI	It can oxidise colourless HBr to produce red Br_2 and HI to give free iodine.	It cannot oxidise HBr or HI.

• Comparison of the properties of sulphurous acid and sulphuric acid.

Properties	Sulphurous acid (H_2SO_3)	Sulphuric acid (H_2SO_4)
(1) Stability	Unstable acid it has never been isolated in the pure form. It is known only in its aqueous solution.	Very stable acid.
(2) Acid property	Weak dibasic acid. Its aqueous solution on being slightly heated gives off SO_2. It gives two types of salts—normal salt (sulphite) and acid salt (bi-sulphite)	A strong dibasic acid. It gives two types of salts–normal salt (sulphates) and acid salt (bi-sulphates)
(3) Oxidising	Exhibits oxidising property. It can oxidise H_2S to produce sulphur. $2H_2S + H_2SO_3 = 3H_2O + 3S\downarrow$	A strong oxidising agent. It can oxidise metals, non metals and compounds. $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$ $C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$
(4) Reducing property	This acid exhibits reducing property. It reduces red coloured Br_2 water into colourless HBr. $Br_2 + H_2SO_3 + H_2O = 2HBr + H_2SO_4$	Sulphuric acid does not possess any reducing property.
(5) Action of heat.	On being heated in a sealed tube at 150°C, a part of the acid is oxidised to give H_2SO_4 and the other part is reduced to sulphur. $3H_2SO_3 = 2H_2SO_4 + S + H_2O$	Conc. H_2SO_4 on being strongly heated decomposes to give SO_2 and O_2 $2H_2SO_4 = 2H_2O + 2SO_2 + O_2$
(6) Dehydrating action	Cannot absorb water or abstract elements of water from other substances.	A strong dehydrating agent. It can absorb water of crystallisation from blue vitriol yielding white anhydrous $CuSO_4$. It can abstract elements of water from organic compounds. $C_{12}H_{22}O_{11} + [H_2SO_4] \rightarrow 12C + [11H_2O + H_2SO_4]$

• Thiosulphuric acid ($H_2S_2O_3$) and thiosulphates :

Thiosulphuric acid is known only in aqueous solution.

(1) It is prepared by the action of *sodium thiosulphate* on very dil. HCl.

$$Na_2S_2O_3 + HCl = H_2S_2O_3 + 2NaCl.$$

The acid is very unstable and easily decomposes to sulphur dioxide and free sulphur.

$$H_2S_2O_3 = H_2O + SO_2 + S\downarrow$$

The salts of thiosulphuric acid is known as *thiosulphates*.

• Sodium thiosulphate :

(i) Sodium thiosulphate is prepared by boiling a concentrated solution of *sodium sulphite* with excess of *sulphur*. This salt is termed as *hypo* by photographers.

$$Na_2SO_3 + S = Na_2S_2O_3$$

The resulting solution is filtered and the filtrate on being evaporated and cooled yields crystals of sodium thiosulphate.

(ii) Pure sodium thiosulphate is obtained by the action of *sodium hydrosulphide* and *sodium bisulphite* in aqueous solution.

$$2NaHS + 4NaHSO_3 = 3Na_2S_2O_3 + 3H_2O$$

The resulting solution is filtered, concentrated and allowed to cool when colourless monoclinic crystals of $Na_2S_2O_3, 5H_2O$ separate out.

Properties : (i) *Action on dilute acids :* On being heated with dilute HCl, *thiosulphuric acid* is first produced which decomposes immediately to *sulphur dioxide* and *sulphur*.

$$\begin{array}{c} Na_2S_2O_3 + 2HCl = 2NaCl + H_2S_2O_3 \\ H_2S_2O_3 = H_2O + SO_2 + S \\ \hline Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O \end{array}$$

(ii) *Action on silver nitrate :* With silver nitrate solution, dilute solution of sodium thiosulphate forms a *white precipitate* of *silver thiosulphate* which turns black due to the formation of *silver sulphide*.

$$2AgNO_3 + Na_2S_2O_3 = Ag_2S_2O_3 \downarrow + 2NaNO_3$$
$$Ag_2S_2O_3 + H_2O = Ag_2S \downarrow + H_2SO_4$$

The white precipitate of $Ag_2S_2O_3$ dissolves on addition of excess of $Na_2S_2O_3$ due to the formation of the complex *sodium argento thiosulphate.*

$$Ag_2S_2O_3 + 3Na_2S_2O_3 = 2Na_3[Ag(S_2O_3)_2]$$

(iii) Solution of sodium thiosulphate dissolves silver halides (AgCl, AgBr, AgI) with the formation of colourless complex sodium argento thiosulphate.

$$AgBr + 2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2] + NaBr$$

This property of sodium thiosulphate is utilised in the 'fixing' of the negatives in photography as it removes the unchanged AgBr from the negatives.

(iv) It decolourises a solution of iodine when it is oxidised to give a quantitative yield of *sodium tetra thionate.*

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

(v) Solution of $Na_2S_2O_3$ decolourises the potassium *permanganate solution* to produce *colourless manganous salt* itself being oxidised to Na_2SO_4.

$$2KMnO_4 + 3H_2SO_4 + 5Na_2S_2O_3 = K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 3H_2O + 5S \downarrow$$

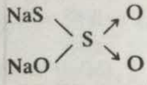
(vi) $Na_2S_2O_3$ solution gives a white precipitate of *barium thiosulphate* with $BaCl_2$ solution. This white precipitate dissolves in HNO_3.

When 2 or 3 drops of ferric thiosulphate are added to $Na_2S_2O_3$ solution at first a violet colour appears due to the formation of ferric thiosulphate, but it disappears quickly as $FeCl_3$ is reduced by $Na_2S_2O_3$ to $FeCl_2$.

$$3Na_2S_2O_3 + 2FeCl_3 \rightleftharpoons Fe_2(S_2O_3)_3 + 6NaCl$$
$$2FeCl_3 + 2Na_2S_2O_3 = 2FeCl_2 + Na_2S_4O_6 + 2NaCl$$

- **Uses :** It is used—(i) in photography, (ii) in textile industry as antichlor, (iii) in the extraction of gold and silver, (iv) for the estimation of iodine.

- **Structure :**



- **Per disulphuric acid ($H_2S_2O_8$ — Marshall's acid) :**

Preparation — by the anodic oxidation of H_2SO_4.

Perdisulphuric acid is prepared by the electrolysis of ice cold 50% sulphuric acid, using a platinum anode and copper wire as cathode. 50% sulphuric acid in ice cold condition is taken in a wide test tube. A platinum wire is dipped into the acid which acts as anode. A spiral copper wire is wound round a glass tube which surrounds the anode. On electrolysis hydrogen is liberated at the cathode and perdisulphuric acid is produced at the anode.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

At cathode : $2H^+ + 2e = H_2$, At anode : $2HSO_4^- - 2e = 2HSO_4$; $2HSO_4 = H_2S_2O_8$

Properties : (i) It is stable and decomposes on heating evolving oxygen.

$$2H_2S_2O_8 = 2H_2SO_4 + 2SO_3 + O_2$$

(ii) Perdisulphuric oxidises (a) ferrous sulphate to ferric sulphate.

$$2FeSO_4 + H_2S_2O_8 = Fe_2(SO_4)_3 + H_2SO_4$$

(b) It oxidises SO_2 to H_2SO_4 and iodides to iodine.

$$SO_2 + H_2S_2O_8 + 2H_2O = 3H_2SO_4, \quad 2KI + H_2S_2O_8 = K_2SO_4 + H_2SO_4 + I_2$$

(c) It oxidises hydrochloric acid to chlorine.

$$2HCl + H_2S_2O_8 = 2H_2SO_4 + Cl_2$$

(iii) *Acid property :* It reacts with KOH or NaOH producing per disulphates. It is dibasic acid.

$$2NaOH + H_2S_2O_8 = Na_2S_2O_8 + 2H_2O$$

(iv) *Bleaching action :* The acid and the perdisulphates have bleaching property.

(v) With water it produces sulphuric acid and H_2O_2.

$$H_2S_2O_8 + 2H_2O = H_2O_2 + 2H_2SO_4$$

- **Uses :** It is used—(i) in the manufacture of H_2O_2, (ii) as a bleaching agent and as an oxidising agent.

- **Permonosulphuric acid (H_2SO_5 — Caro's acid) :**

Preparation : Powdered potassium per disulphate is mixed with ice cold conc. H_2SO_4 and the mixture is added to ice when an aqueous solution of permono sulphuric is produced. On further cooling crystals of permono sulphuric acid are obtained.

$$K_2S_2O_8 + H_2SO_4 = H_2S_2O_8 + K_2SO_4$$
$$H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5$$

(ii) It is also prepared by the action of chloro sulphonic acid on hydrogen peroxide

$$H—O—O\boxed{H + Cl}—SO_2HO \quad = \quad HO—O—SO_2—OH + HCl$$

Properties : It is colourless crystalline solid. It is hygroscopic and soluble in water.

(i) On being treated with H_2O_2 it liberates O_2.

$$H_2SO_5 + H_2O_2 = H_2SO_4 + H_2O + O_2$$

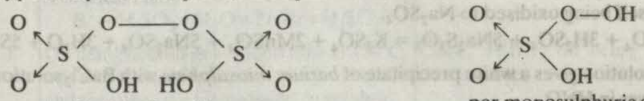
(ii) It is an oxidising agent. It oxidises KI to iodine.

$$2KI + H_2SO_5 = K_2SO_4 + I_2 + H_2O$$

(iii) On being distilled with dilute H_2SO_4 it forms H_2O_2.

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$$

Structures of perdisulphuric and permono sulphuric acid.



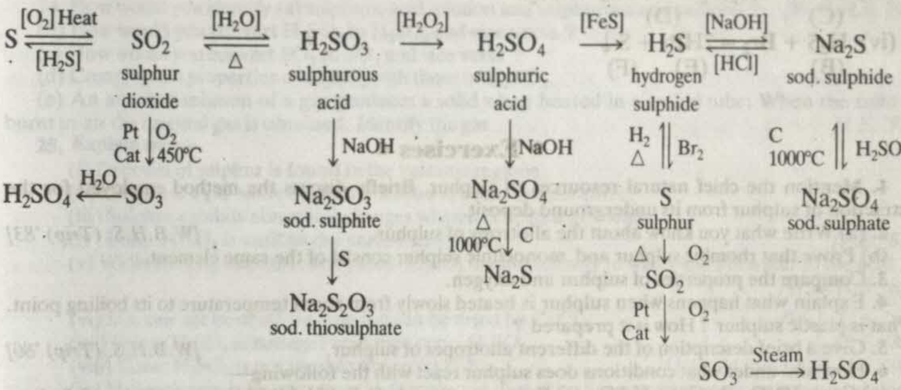
per disulphuric acid

per monosulphuric acid

- **Distinguishing tests for $S^{=}$, $SO_3^{=}$, $SO_4^{=}$ and $S_2O_3^{=}$.**

Tests	Sulphide	Sulphite	Sulphate	Thiosulphate
1. Action of dil. HCl	H_2S is liberated which has a smell of rotten egg and which turns lead acetate paper black	SO_2 is liberated which has a smell of burning sulphur and which turns dichromate paper green	No gas evolves.	SO_2 gas is evolved which turns dichromate paper green and yellow ppt of S is obtained
2. Action of $BaCl_2$ solution	No ppt is formed	White ppt of $BaSO_3$ is obtained which dissolves in HNO_3 but reappears on addition of bromine water.	White ppt of $BaSO_4$ is obtained which is insoluble in HNO_3	White ppt of BaS_2O_3 is obtained which dissolves in HNO_3 producing the ppt of S.
3. Action of silver nitrate solution.	Black ppt of Ag_2S is obtained which is soluble in hot and dil. HNO_3	A white ppt of Ag_2SO_3 is obtained which is soluble in HNO_3	No ppt is obtained	A white ppt of $Ag_2S_2O_3$ is obtained which turns black due to the formation of Ag_2S.
4. Action of $FeCl_3$ solution.	A black ppt of FeS is obtained	The solution turns dark red.	No action	The solution turns violet which disappears soon.
5. To the aqueous solution Na-nitroprusside soln. is added	The colourless solution turns violet	No action	No action	No action
6. To the solution lead acetate soln. is added	The solution turns black due to the formation of PbS	No action	A white ppt is obtained which is soluble in ammonium acetate	No action

- **Conversion sulphur into different compounds :**



- **Some problems regarding the reactions of S and its compounds.**

1. *Conc. H_2SO_4 on being heated with metallic Cu yields a gas (A). When (A) gas is passed through iodine suspended in water two acids (B) and (C) are obtained. On adding $BaCl_2$ solution. to this mixture of acids a white ppt. (D) is obtained, which is insoluble in HNO_3. (B) when heated with conc. H_2SO_4 yields (A) and another violet coloured gas (E). Identify A, B, C, D and E.*

Ans : A = sulphur dioxide (SO_2), B = hydroiodic acid, C = sulphuric acid, D = barium sulphate and E = iodine.

Reactions : (i) $Cu + 2H_2SO_4 \xrightarrow[\Delta]{} CuSO_4 + \underset{(A)}{SO_2} \uparrow + 2H_2O$

(ii) $SO_2 + I_2 + 2H_2O = \underset{(B)}{2HI} + \underset{(C)}{H_2SO_4}$

(iii) $H_2SO_4 + BaCl_2 = \underset{(D)}{BaSO_4} \downarrow + 2HCl$

(iv) $2HI + H_2SO_4 = \underset{(E)}{I_2} + \underset{(A)}{SO_2} + 2H_2O.$

2. *The aqueous solution of a gas produces a solid when heated in a sealed tube. When the solid is burnt in air the original gas is obtained. Identify the gas.* *[Jt. Ent. 92]*

Ans : The gas is sulphur dioxide.

As, the aqueous solution of SO_2 i.e., H_2SO_3 when heated in a sealed tube, at 150°C, sulphur is precipitated.

$$3H_2SO_3 = 2H_2SO_4 + S \downarrow + H_2O.$$

The sulphur thus obtained when burnt in air, it combines with the O_2 of air to form the original gas i.e., SO_2.

$$S + O_2 = SO_2 \uparrow$$

3. *A sodium salt (A) reacts with dilute HCl to evolve a colourless gas (B). (B) when passed through lead acetate solution, a black precipitated (C) is obtained. (C) on being treated with H_2O_2 yields a white substance (D). (B) gas when passed through bromine water yields a colourless acid (E) and a yellow precipitated (F). (F) is soluble in CS_2. Identify A, B, C, D, E and F.*

Ans : A = sodium sulphide ; B = hydrogen sulphide ; C = lead sulphide ; D = lead sulphate ; E = hydrobromic acid ; F = sulphur.

Reactions : (i) $\underset{(A)}{Na_2S} + 2HCl = 2NaCl + \underset{(B)}{H_2S}$

$$\text{(ii)}\ \underset{(B)}{H_2S} + (CH_3COO)_2Pb = 2CH_3COOH + \underset{(C)}{PbS}\downarrow$$

$$\text{(iii)}\ \underset{(C)}{PbS} + 4H_2O_2 = \underset{(D)}{PbSO_4} + 4H_2O$$

$$\text{(iv)}\ \underset{(B)}{H_2S} + Br_2 = \underset{(E)}{2HBr} + \underset{(F)}{S}\downarrow$$

• Exercises •

1. Mention the chief natural resources of sulphur. Briefly discuss the method employed for the extraction of sulphur from its underground deposit.

2. (a) Write what you know about the allotropy of sulphur. *[W.B.H.S. (Trip) '83]*

(b) Prove that rhombic sulphur and monoclinic sulphur consist of the same element.

3. Compare the properties of sulphur and oxygen.

4. Explain what happens when sulphur is heated slowly from room temperature to its boiling point. What is plastic sulphur ? How is it prepared ?

5. Give a brief description of the different allotropes of sulphur. *[W.B.H.S. (Trip) '80]*

6. How and under what conditions does sulphur react with the following—

(a) Conc. HNO_3, (b) Conc. H_2SO_4, (c) Excess caustic soda *[J.E. 85]*, (d) Chlorine, (e) Coke, (f) Sodium sulphite *[J.E. 85]*, (g) Hydrogen.

7. Starting from sulphur how would you prepare (i) $NaHSO_3$, (ii) H_2S, (iii) $Na_2S_2O_3$, (iv) FeS, (v) SO_2, (vi) Na_2SO_4 ?

8. (a) How would you prepare sulphur dioxide in the laboratory ? *[J.E. '84 ; W.B.H.S. '89]*

(b) Prove that sulphur dioxide contains sulphur. *[W.B.H.S. '86]*

(c) Illustrate giving equations to show that sulphur dioxide acts both as an oxidising and reducing agent. *[J.E. '87]*

9. Compare the properties of SO_2 with those of CO_2. *[W.B.H.S. (Trip) '84]*

10. Discuss the principles how Cl_2 and SO_2 act as bleaching agents. *[W.B.H.S. '90]*

11. (a) How would you separate CO_2 from a mixture of SO_2 and CO_2 ? *[J.E. '87]*

(b) Compare the bleaching action of sulphur dioxide and chlorine.

(c) Both SO_2 and CO_2 turns lime water milky. How would you detect the presence of CO_2 in the mixture ?

12. Describe the preparation of sulphur trioxide in the laboratory. Illustrate its oxidising property.

13. Starting from sulphur how would you prepare sulphurous acid ? *[W.B.H.S. '80]*. Show that sulphurous acid is dibasic.

14. Prove that (i) SO_3 is an acidic oxide, (ii) H_2SO_3 contains sulphur, (iii) H_2SO_3 has both the oxidising and reducing property.

15. How would you prepare an aqueous solution of sulphurous acid ? Discuss its acid property and oxidising property with suitable examples. How would you detect a sulphite salt ?

16. (a) Discribe the laboratory method of preparation of hydrogen sulphide.

(b) How would you obtain sulphur from hydrogen sulphide and vice versa ?

(c) How with the help of a Kipp's apparatus, a ready supply of hydrogen sulphide is obtained in the laboratory. Explain it with a sketch. *[W.B.H.S. '91]*

17. (a) How would you obtain hydrogen sulphide from (i) sodium sulphate *[W.B.H.S. '89]*, (ii) sulphur, (iii) sodium thiosulphate ?

(b) How would you distinguish between sodium sulphate and sodium sulphite ? *[W.B.H.S. '84]*

18. Describe with a neat diagram how Kipp's apparatus is used for the occasional preparation of H_2S whenever required in the laboratory. *[H.S. '89]*

19. Discuss the uses of H_2S as a reagent in the qualitative analysis of basic radicals.

20. (a) Illustrate some chemical reactions to prove the reducing property of hydrogen sulphide.

(b) Starting from H_2S how would you prepare (i) SO_2, (ii) S, (iii) H_2SO_4, (iv) $Na_2S_2O_3$?

21. (a) Describe the laboratory method of preparation of sulphuric acid, Mention some important uses of sulphuric acid. Give an example of the dehydrating action of H_2SO_4. *[H.S. '94]*

(b) Mentioning the names of the compounds show that the oxidation number of sulphur may be positive or negative. *[J.E. '83] [H.S. '94]*

(c) What is oleum ?

22. Prove that—conc. H_2SO_4 is (i) dibasic acid, (ii) a strong oxidising agent, (iii) a dehydrating agent. Mention two gases which are dried by conc. H_2SO_4 and mention three gases which can not be dried by conc. H_2SO_4.

23. Describe the principles involved in different steps in the manufacture of sulphuric acid by contact process, with special reference to the role of temperature and catalyst. Why a pressure higher than the normal atmospheric pressure is not used in the process ? *[W.B.H.S. '86, '88, '90, '91]*

24. How would you identify (a) sulphuric acid solution and sulphurous acid solution ? *[W.B.H.S. '81]*

(b) How would you convert H_2SO_3 to H_2SO_4 and vice versa ?

(c) How would you convert SO_2 to SO_3 and vice versa ?

(d) Compare the properties of H_2SO_4 with those of H_2SO_3.

(e) An aqueous solution of a gas produces a solid when heated in a sealed tube. When the solid is burnt in air the original gas is obtained. Identify the gas. *[J.E. '91]*

25. Explain why—

(i) Deposits of sulphur is found in the volcanic regions.

(ii) Oxygen is a gas while sulphur is a solid at room temperature.

(iii) Sulphur exhibits abnormal changes when it is heated gradually.

(iv) Conc. H_2SO_4 is unfit to dry carbon monoxide. *[J.E. '87]*

(v) While diluting sulphuric acid, conc. H_2SO_4 is added slowly to water and not water to the acid. *[W.B.H.S. '85]*

(vi) SO_2 can not be dried by lime but can be dried by $CaCl_2$. *[W.B.H.S. '85]*

(vii) Dilute H_2SO_4 is stronger acid than conc. H_2SO_4. *[J.E. '80]*

(viii) Conc. H_2SO_4 is not used to dry moist H_2S. *[J.E. '84, '90, W.B.H.S. '93]*

(ix) H_2S molecule is heavier than H_2O molecule, but at ordinary temperature hydrogen sulphide is a gas while water is liquid. *[J.E. 83, 90]*

(x) SO_2 can act as an oxidant as well as a reductant but CO_2 acts only as an oxidising agent. *[J.E. '83, W.B.H.S. '86, '88]*

(xi) HBr or HI can not be dried by conc. H_2SO_4. *[W.B.H.S. '85]*

(xii) Nitric acid or conc. H_2SO_4 is not used in the preparation of hydrogen sulphide from FeS. *[J.E. '87]*

(xiii) In the manufacture of H_2SO_4 by contact process, SO_3 is absorbed by 88% H_2SO_4 instead of absorbing it in water. *[J.E. '84]*

(xiv) H_2S can reduce only but can not oxidise.

(xv) Conc. H_2SO_4 can oxidise only but can not reduce.

(xvi) Sugar is charred by conc. H_2SO_4.

(xvii) H_2SO_4 can not be prepared by heating Na_2SO_4 with conc. HCl or conc. HNO_3.

(xviii) Conc. H_2SO_4 or fused $CaCl_2$ is not employed to dry hydrogen sulphide.

(xix) SO_2 can form additive compounds but CO_2 cannot.

(xx) In the preparation of H_2SO_4 by contact process the catalyst is initially heated, but once the reaction starts the external source of heat is removed.

(xxi) Dry flower cannot be bleached by SO_2.

(xxii) Sulphur melts to clear mobile liquid at 119°C, but on further heating above 160°C, it becomes viscous.

(xxiii) SO_2 molecule is polar but CO_2 molecule is not polar. *[Jt. Ent. '83]*

(xxiv) H_2SO_4 is stronger acid than H_2SO_3.

(xxv) Dilute H_2SO_4 is a better conductor of electricity than conc. H_2SO_4.

(xxvi) Aqueous solution of H_2S when kept exposed in air turns turbid.

(xxvii) Dilute H_2SO_4 can not be made concentrated by evaporation above a certain limit. *[Jt. Ent '85]*

(xxviii) SO_2 can not bleach in absence of moisture. *[W.B.H.S. '85*

(xxix) HBr can not be prepared by the action of conc. H_2SO_4 or NaBr. *[W.B.H.S. '85]*

(xxx) H_2S is better reducing agent than water.

(xxxi) H_2O is thermally more stable than H_2S.

(xxxii) Conc. H_2SO_4 is viscous and has high boiling point.

(xxxiii) Wooden shelf under the reagent bottle containing conc. H_2SO_4 blackens after some time.

(xxxiv) We feel a pungent smell when a match stick starts burning.

26. Prove that—

(i) Hydrogen sulphide contains sulphur and hydrogen.

(ii) Sulphur dioxide contains sulphur.

(iii) Sulphuric acid contains hydrogen, sulphur and oxygen. *[H.S. '94]*

(iv) Sodium sulphate contains sulphur.

(v) Sodium thiosulphate contains sulphur.

(vi) Potassium sulphite contains sulphur.

(vii) Ferrous sulphide contains sulphur.

27. (a) How would you separate—

(i) CO_2 from a mixture of SO_2 and CO_2.

(ii) SO_2 from a mixture of CO_2 and SO_2.

(iii) H_2S from a mixture of H_2 and H_2S.

(iv) H_2S from a mixture of SO_2 and H_2S.

(b) Which one will you prefer—conc. H_2SO_4 or conc. HCl, for the flame test ? *[J.E. '87]*

(c) Which of the following , compounds of sulphur acts (i) only as a reductant, (ii) only as an oxidant, (iii) as both oxidant and reductant ?

(i) H_2S, (ii) SO_2, (iii) H_2SO_4 *[J.E. '89]*

28. State what happens when (with visual changes if any) :

(i) SO_2 is passed over red hot coke. *[J.E. '87]*

(ii) Powdered sulphur is boiled with conc. HNO_3. *[W.B.H.S. '84, '89]*

(iii) To a mixture of sodium nitrate and ferrous sulphate conc. H_2SO_4 is slowly added. *[J.E. '89]*

(iv) Solid Na_2SO_3 is heated with dil. HCl and the evolved gas is passed through $K_2Cr_2O_7$ solution acidified with H_2SO_4. *[W.B.H.S. '83, '90]*

(v) Dil. H_2SO_4 is added to ferrous sulphide and a filter paper soaked in lead acetate solution is held in the evolved gas. *[W.B.H.S. '90]*

(vi) Chlorine is passed through an aqueous solution of SO_2. *[W.B.H.S. '85]*

(vii) Oxalic acid is heated with conc. H_2SO_4. *[J.E. '83]*

(viii) Conc. H_2SO_4 is allowed to drop on red hot pumice stones. *[J.E. '84]*

(ix) H_2S is passed through conc. H_2SO_4. *[J.E. '84]*

(x) SO_2 is passed through iodine suspended in water.

(xi) H_2S is passed through a mixture of the solutions of $CuCl_2$ and $ZnCl_2$ acidified with dil. HCl. *[W.B.H.S. '85, '91]*

(xii) Sulphur is mixed with sodium sulphite and the mixture is heated. *[W.B.H.S. '85]*

(xiii) Sodium formate is heated with conc. H_2SO_4. *[W.B.H.S. '86]*

(xiv) Ozone gas is reacted with SO_2. *[W.B.H.S. '88]*

(xv) Zinc is reacted with hot and conc. H_2SO_4. *[W.B.J.E. '90]*

(xvi) Excess SO_2 is passed through lime water. *[J.E. '79]*

(xvii) H_2S is passed separately through (a) bromine water, (b) chlorine water.

(xviii) Powdered charcoal or carbon is reacted with hot and conc. H_2SO_4. *[W.B.H.S. '80, '94]*

(xix) Potassium nitrite is added to KI solution acidified with H_2SO_4. *[W.B.H.S..'83]*

(xx) H_2S is passed through an acidified solution of potassium permanganate. *[W.B.H.S. (Trip) '81]*

(xxi) H_2S is passed through acidified ferric chloride solution. *[H.S. (Trip) '83]*

(xxii) Conc. H_2SO_4 is treated with (a) phosphorus, (b) copper, (c) KI, (d) potassium ferrocyanide, (e) formic acid, (f) PCl_5.

(xxiii) 60% H_4SO_4 is electrolysed with platinum electrodes.

(xxiv) Sodium thiosulphate is treated with iodine.

(xxv) Sulphur is boiled with caustic soda. *[Roorkee Eng. '88]*

(xxvi) Hydrogen sulphide is bubbled through an aqueous solution of SO_2. *[I.I.T. '85]*

(xxvii) Sulphur is precipitated in the reaction of H_2S with sodium bisulphite solution. *[I.I.T. '91]*

Hints : $NaHSO_3 + H_2S + HCl = NaCl + 3S\downarrow + 3H_2O$.

(xxviii) Aqueous solution of $KMnO_4$ is mixed with sulphuric acid. *[I.I.T. '84]*

(xxix) Aqueous solution of $K_2Cr_2O_7$ is mixed with sulphuric acid. *[I.I.T. '84]*

(xxx) Ferrous sulphate and $K_2Cr_2O_7$ react in presence of dil. H_2SO_4.

(xxxi) hypo solution is treated with $AgNO_3$ solution.

(xxxii) SO_2 gas, water vapour and air are passed over heated sodium chloride. *[I.I.T. '86]*

Hints : $SO_2 + H_2O + 1/2O_2\,(air) = H_2SO_4$.

$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$.

(xxxiii) Gas evolved by treating Na_2S with water is passed into amoniacal $ZnCl_2$ solution. What is colour and composition of the precipitate ? What happens when the precipitate is treated with HCl followed by NaOH solution ? *[Jt. Ent. '91]*

(xxxiv) H_2S is passed through freshly prepared sodium nitro prusside solution. *[Jt. Ent. '92]*

(xxxv) NO_2 is passed into conc. H_2SO_4.

(xxxvi) SO_2 is passed through a solution of $FeCl_3$ containing HCl.

29. Describe with equations how would you convert the following —

(a) H_2SO_4 from H_2SO_3 and vice versa. (b) Na_2SO_4 from H_2S *[W.B.H.S. '89]* (c) Rhombic sulphur from monoclinc sulphur and vice versa *[Jt. Ent. '92]*(d) Sulphur dioxide from Na_2SO_4 (e) SO_2 from SO_3 and vice versa. (f) H_2SO_4 from SO_2 (g) Sodium thiosulphate from Na_2SO_4 *[I.I.T. '82]* (h) Sulphur from H_2SO_4 (i) Hypo from Na_2CO_3 (j) H_2SO_4 from sulphur.

30. Give one chemical reaction for each to distinguish between —

(i) Na_2SO_4 and Na_2SO_3 *[W.B.H.S. '82]* (ii) H_2SO_4 and H_2SO_3 (iii) CO_2 and SO_2 (iv) H_2S and SO_2 (v) Na_2S and Na_2SO_3 (vi) $Na_2S_2O_3$ and Na_2SO_3 (vii) SO_2 and SO_3.

31. Describe this physico-chemical process of preparation of H_2SO_4 by contact process. *[H.S. '94]*

32. (a) A solution of salt becomes violet on addition of Na nitro prusside. Identify the acid radical.

(b) State the bond angle present in H_2O and H_2S.

30. Objective type questions : Among the various alternatives given below each sub question, choose the correct one(s).

(1) SO_2 is— (a) an oxidising agent, (b) an acidic oxide, (c) a reducing agent, (d) all the above. [***Ans.*** (d)]

(2) In the preparation of sulphur di-oxide by the action of copper on conc. H_2SO_4, the acid used as— (a) an oxidising agent, (b) a reducing agent, (c) a dibasic acid, (d) a drying agent. [***Ans.*** (a)]

(3) Caro's acid is— (a) $H_2S_2O_8$, (b) H_2SO_5, (c) $H_2S_2O_7$, (d) $H_2S_2O_3$. [***Ans.*** (b)]

(4) The acid chloride of H_2SO_4 is— (a) $SOCl_2$, (b) SO_2Cl_2, (c) S_2Cl_2, (d) none of these. [***Ans.*** (d)]

(5) The reaction $C + SO_2 = CO_2 + S$ shows that— (a) C is a reducing agent, (b) SO_2 contains sulphur, (c) SO_2 is an oxidising agent, (d) all the above. [***Ans.*** (d)]

(6) Which of the following liberates CO_2 on heating with conc. H_2SO_4 ?
(a) ethanol, (b) formic acid, (c) $K_4Fe(CN)_6$, (d) oxalic acid. [***Ans.*** (d)]

(7) Hypo is— (a) $Na_2SO_4, 10H_2O$, (b) $Na_2S_2O_3, 5H_2O$, (c) Na_2S. [***Ans.*** (b)]

(8) Which of the following is essential for the bleaching action of SO_2 ?
(a) presence of O_2, (b) presence of moisture, (c) presence of active charcoal, (c) presence of sun light. [***Ans.*** (b)]

(9) In the contact process SO_3 is absorbed by— (a) water, (b) dil. H_2SO_4, (c) 98% H_2SO_4, (d) dil. HNO_3. [***Ans.*** (c)]

(10) Which of the following turns acidified $KMnO_4$ solution colourless ?—
(a) Na_2SO_4, (b) SO_3, (c) H_2SO_4, (d) SO_2. [***Ans.*** (d)]

(11) H_2SO_3 gives two series of salts because— (a) it is an weak acid, (b) it is a strong acid, (c) it is dibasic acid, (d) it is unstable. [***Ans.*** (c)]

(12) Conc. H_2SO_4 does not oxidise— (a) HBr, (b) H_2S, (c) HCl (d) HI. [***Ans.*** (c)]

(13) H_2SO_4 does not match with— (a) sulphate, (b) oxidising agent, (c) contact process, (d) bleaching agent. [***Ans.*** (d)]

(14) The highest oxidation number of sulphur is in— (a) S, (b) H_2S, (c) SO_3, (d) SO_2, (e) $H_2S_2O_3$. [***Ans.*** (c)]

(15) Conc. H_2SO_4 chars sugar by— (a) reduction, (b) oxidation, (c) dehydration, (d) sulphonation.

(16) Conc. H_2SO_4 connot be used for drying— (a) NH_3, (b) HCl, (c) Cl_2, (d) N_2. [***Ans.*** (a)]

(17) Sulphuric acid forms— (a) sulphides, (b) sulphates, (c) sulphites, (d) thiosulphates. [***Ans.*** (b)]

(18) Blue crystals of $CuSO_4$ turns white in presence of— (a) conc. HCl, (b) conc. HNO_3, (c) conc. H_2SO_4, (d) H_2SO_3. [***Ans.*** (c)]

(19) Which of the following statements is not true regarding H_2SO_4 ?
(a) It is an oxidising agent, (b) It is a monobasic acid, (c) It is a strong acid, (d) It is a dehydrating agent. [***Ans.*** (b)]

(20) Which of the folowing metals can not displace H_2 from dil. H_2SO_4 ?
(a) Zinc (b) Iron (c) Copper (d) Magnesium. [***Ans.*** (c)]

7

Halogens and their Hydracids

The five elements, viz., *fluorine, chlorine, bromine, iodine* and *astatine* have been placed in Group VIIB in the periodic table. The four elements—*fluorine, chlorine, bromine* and *iodine* form a family of closely related elements and are collectively known as *halogens.* The term halogen has come from the Greek *'hales'* (=sea salt) and *'geno'* (=I produce) meaning literally sea salt producers, because most of these elements occur in sea water as sodium compounds. The binary compounds of the halogens with other elements are called *halides.*

• FLUORINE •

Symbol—F	**Atomic No.—9**	**Atomic weight.=19.02**
Electronic configuration : $1s^2 2s^2 2p^5$		**Oxidation No. (−1)**

• Anomalous behaviour of fluorine :

Fluorine is the first member of Group VIIB and so it differs considerably from the other members of the group. This is due to– (i) the small size of fluorine atom, (ii) its high electronegativity ; and (iii) the absence of '*d*' orbitals in its valence shell.

Fluorine differs from the other halogens in the following aspects—

(i) **Reactivity :** Due to its high electronegativity and low F—F bond dissociation energy, fluorine is the most reactive element among the other halogens as represented below —

(a) It displaces other halogens from the corresponding halides.

(b) It decomposes water violently and liberates ozonised oxygen.

(c) It can combine directly with carbon while other halogens do not react with carbon directly.

(d) It reacts with other halogens.

(e) It forms strong bonds with other elements and thus forms stable compounds. Thus UF_6 is more stable than UCl_6. NF_3 is not explosive while NCl_3 is highly explosive.

(ii) **Formation of hydrogen bonding :** Due to the high electronegativity and small size of fluorine atom, hydrogen bonding occurs in HF, while it is absent in other halogen acids. Because of the presence of hydrogen bonding in HF, it is liquid below 19·5°C with abnormally high boiling point, while other halogen acids are gaseous. For the presence of H-bond *hydrogen fluoride behaves as a dibasic acid (H_2F_2) and can form acid salt like KHF_2. The other halogen acids are monobasic* and cannot form such compounds.

(iii) **Oxidation states :** Fluorine being the most electronegative element, exhibits only a negative oxidation state of (−1) while the other members show negative as well as positive oxidation states e.g., (−1), (+1), (+3), (+5) and (+7).

(iv) **Strength of hydracids :** Fluorine forms highly associated hydracid HF due to the presence of extensive hydrogen bonding between its molecules and as a result HF ionises slightly in water and behaves as a weak acid while the hydracids of other halogens are strong as they are not associated due to the absence of hydrogen bonding between their molecules. HI is the strongest acid among the hydracids.

(v) **Formation of oxyacids :**

- *Fluorine does not have any oxyacid.*

Fluorine differs from the other halogens in forming no oxyacid or oxysalt. This is due to the fact that in all oxides, oxygen occurs as the most electronegative part of the binary compound. But since fluorine is the most electronegative element, oxygen is more electropositive compared to fluorine. Consequently the binary compound of fluorine and oxygen OF_2 will be a fluoride and not an oxide. Oxyacids have a corresponding anhydride, since fluorine has no oxide—it can not have any oxyacids like other halogens. As the other halogens (Cl, Br, I) are less electronegative than oxygen, they can form oxides and oxyacids. Again all oxyacids of halogens are stabilised by $d\pi - p\pi$ bond. Since F has no *d* orbital such stabilisation would not occur. Hence Fluorine cannot form any oxyacids.

(vi) **Solubility of salts :** Fluorine differs from the rest of the halogens in respect of its two salts, viz., *silver fluoride* is soluble in water whereas AgCl, AgBr, AgI are insoluble. *CaF_2 is insoluble in water* while $CaCl_2$, $CaBr_2$ and CaI_2 are extremely soluble.

(vii) **Action on water :** Fluorine decomposes water to produce oxygen and ozone.

$$2F_2 + 2H_2O = 4HF + O_2 \; ; \qquad 3F_2 + 3H_2O = 6HF + O_3$$

(viii) Fluorine does not form any poly halides while other halogens can form poly halides e.g., I_3, Br_3. This is due to the absence of *'d'* orbitals in the valency shell of F atom.

(ix) Fluorides have maximum ionic character than the other halides. Thus AlF_3 and SnF_4 are ionic while other halides of Al and Sn (iv) are covalent.

(x) **Low electron affinity :** Although F is more electronegative than Cl, its electron affinity is lower than that of Cl atom. Due to the very small size of F atom, its electron density becomes high and as a result its electron affinity becomes low. (See volume 2).

7·1. Occurrence of fluorine.

Fluorine is highly reactive element and so it does not occur in free state. It is found in nature in a combined state as *fluorides*. The chief minerals of fluorine are—

(i) *Fluorspar* (CaF_2), (ii) *Cryolite* (AlF_3, $3NaF$), (iii) *Fluor apatite* [$3Ca_3(PO_4)_2$, CaF_2].

Small quantities of fluorine are found to be in sea water and in bones and in the teeth of animals as fluoride.

• Isolation of fluorine.

Scheele in 1771 produced hydrofluoric acid by distilling a mixture of fluospar (CaF_2) and conc. H_2SO_4. In 1893 *Davy* was the first to observe the similarities of the properties of HF with those of HCl and he proved the existence of an unknown element combined with hydrogen in hydrofluoric acid.

Davy tried to isolate this unknown element *by the electrolysis of an aqueous solution of hydrofluoric acid just as chlorine could be obtained by the electrolysis of the aqueous solution of HCl. But due to the extreme chemical reactivity and high electronegativity of fluorine, oxygen and ozone were liberated at the anode instead of the new element. Again due to its high electronegativity, it was not posssible to oxidise HF to fluorine by any chemical reagent.* As a result the isolation of fluorine could not be achieved for a long time.

• Why did all earlier attempts of isolation of fluorine fail ?

The main difficulties of isolation of fluorine are given below—

(i) Attempts were made to isolate fluorine by the electrolysis of the aqueous solution of hydrofluoric acid like that of chlorine from hydrochloric acid. But this method of preparation of fluorine failed, as on the electrolysis of aqueous solution of HF, ozonised oxygen was liberated at the anode instead of fluorine. This was because of the fact that fluorine liberated during the electrolysis, immediately reacted with water to produce HF and ozonised oxygen.

$$2H_2O + 2F_2 = O_2 + 4HF, \qquad 3H_2O + 3F_2 = O_3 + 6HF$$

(ii) Because of the high electronegativity of fluorine and great stability of HF, it failed to be oxidised by any oxidising agent. The only possible method was the electrolytic oxidation of HF, but as anhydrous HF was a non conductor of electricity, it could not be electrolysed to yield fluorine.

(iii) The high reactivity of fluorine was the main cause of its late discovery. Due to its high reactivity it attacked the materials (glass, carbon or platinum) of the apparatus used. Consequently it was not possible to obtain fluorine by the electrolysis of fused fluorides such as KF. The electrolytic cell and electrodes made of materials resistant to fluorine, were not available at that time.

(iv) Fluorine as well as hydrofluoric acid being highly poisonous became fatal to many chemists who attempted its isolation.

(v) *Fluorine could not be prepared by the chemical oxidation of hydrofluoric acid or any fluoride.* This is due to the fact that fluorine is the most electronegative element. According to Pauling scale its electronegativity is 4, and the standard reduction potential of fluorine is the maximum of all elements. [$E^\circ_{F_2/2F^-} = +2{\cdot}87$ volts]. Consequently fluorine is the strongest oxidising agent. It is therefore impossible to find out an oxidising agent to oxidise HF or fluoride to fluorine. So fluorine could not be isolated by the oxidation of any fluoride.

(vi) Anhydrous hydrofluoric acid is highly volatile liquid which boils at 19·5°C. Consequently it was necessary to use a suitable refrigerant to kept it in a liquid state during its electrolysis. But a suitable refrigerant to achieve the desired low temperature could not be found at that time.

- **How did Moissan overcome these difficulties ?**

The French chemist *Moissan* was successful in isolating fluorine in 1886 by overcoming all the difficulties mentioned above.

(i) Moissan was the first to show that potassium hydrogen fluoride was soluble in anhydrous hydrofluoric acid and that the solution conducted electricity. So he used anhydrous potassium hydrogen fluoride (20%) dissolved in anhydrous hydrofluoric acid as the electrolyte. The solution was found to be a good conductor of electricity.

(ii) Moissan used an apparatus made of an alloy of platinum and irridium. The electrolytic cell as well as the electrodes were made of the same alloy. It was found that the alloy was much less attacked by fluorine than any other materials.

(iii) In order to keep hydrofluoric acid in a liquid state, Moissan cooled the electrolyte to −23°C by using a bath of boiling *methyl chloride* (b.p. −23°C).

7.2. Preparation of fluorine.

(1) Moissan's method :

[A] Description of the apparatus :

(i) **Electrolytic cell :** The electrolytic cell used by Moissan consisted of a U-tube made of an alloy of platinum and irridium, provided with two side tubes at the upper part of the apparatus.

(ii) **Electrodes :** The open ends of the U-shaped tube were closed with stoppers made of *felspar*. Two electrodes made of platinum-irridium alloy were introduced into the electrolytic cell through the stoppers. The electrodes were thickened at the ends. These electrodes were made insulated from the U-tube by covering the felspar stoppers with shellac.

(iii) **Electrolyte :** A solution of *potassium hydrogen fluoride* KHF_2 (one part) in *anhydrous hydrofluoric acid* HF (5 parts), was taken as electrolyte into the U-tube.

(iv) The electrolytic cell with its contents was cooled to −23°C by immersing it in a bath of boiling methyl chloride which constantly flowed from a reservoir. The bath was provided with an outlet for the escape of the vapours of methyl chloride.

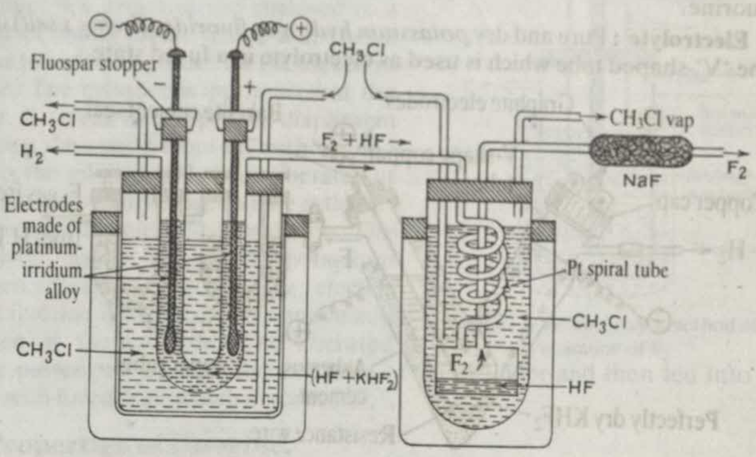


Fig 7.1 : Moissan method of preparation of fluorine

[B] **Procedure :** (i) On passing electric current through the electrolyte, *hydrogen* was liberated *at the cathode* and *fluorine at the anode.* (ii) The liberated fluorine was first led through a platinum spiral tube cooled to −23°C by immersing it into a bath of boiling methyl chloride. Most of the HF vapours present in fluorine were condensed in the spiral tube. (iii) Fluorine gas was next passed through a platinum tube packed with *fused sodium fluoride,* which absorbed the last traces of hydrofluoric acid forming NaHF.

$$NaF + HF = NaHF_2$$

(iv) The fluorine freed from hydrofluoric acid was collected in a gas jar made of platinum-irridium alloy by the upward displacement of air.

[C] **Reaction at the electrodes :**

The reactions at the electrodes are given below—

$$KHF_2 = KF + HF$$

$$KF \rightleftharpoons K^+ + F^-$$

At cathode : $K^+ + e = K.$ $\quad 2K + 2HF = 2KF + H_2\uparrow$

At anode : $F^- - e = F.$ $\quad F + F = F_2\uparrow$

(2) **Modern method of the preparation of fluorine—Dennis method—High temperature process :**

This method was devised by *Dennis* and others in 1931. In this process fluorine is prepared by the electrolysis of fused potassium hydrogen fluoride KHF_2 (sometimes with additional anhydrous hydrogen fluoride) at 240°—250°C. This process is known as high temperature process.

[A] **Description of the apparatus :** The essential parts of the electrolytic cell used in this process are—

(i) **Electrolytic cell :** The electrolytic cell consists of a 'V' shaped copper tube fitted with copper caps into which graphite electrodes are introduced. The 'V' shaped tube is covered all around with an insulating layer of asbestos cement. This asbestos layer is wound by a resistance wire for heating the tube electrically. There are two side tubes in the two arms of the 'V' shaped tube for the escape of hydrogen and fluorine.

(ii) **Electrolyte :** Pure and dry *potassium hydrogen fluoride* (*Fremy's salt*) is taken into the 'V'-shaped tube which is used as electrolyte in a fused state.

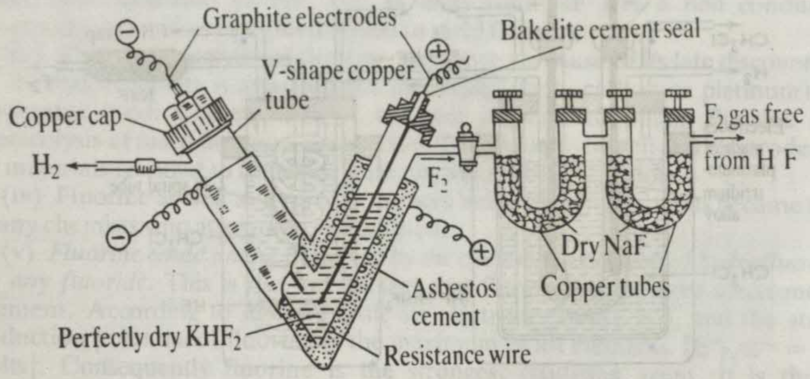


Fig 7.2 : High temperature process (Dennis method) of preparation of fluorine

(iii) **Electrodes :** Two *graphite rods* are introduced into the 'V'-shaped tube which are used as electrodes. The electrodes are insulated by means of bakelite cement stoppers.

[Graphite electrodes are not attacked by fluorine at 250°C]

[B] **Procedure :** The 'V' shaped tube is heated electrically by means of the heating coil to keep the dry KHF_2 inside the vessel in molten condition. Now a current of 5 amperes at 12 volts is passed through the molten potassium hydrogen fluoride, when hydrogen is liberated at the cathode and fluorine at the anode. Fluorine thus liberated at the anode passes out through the exit tube. The liberated fluorine—initially reacts with the inside wall of the copper tube forming a layer of CuF_2 which protects the copper from further attack.

Fluorine thus produced is passed through two copper tubes packed with dry sodium fluoride which absorbs the hydrogen fluoride present in F_2 forming $NaHF_2$. Fluorine thus being freed from HF vapours is collected by the displacement of air in copper gas jar.

[C] **Reaction at the electrodes :**

$$KHF_2 = KF + HF$$

$$KF \rightleftharpoons K^+ + F^-$$

At cathode : $K^+ + e = K$ *At anode :* $2F^- - 2e = F_2\uparrow$

$2K + 2HF = 2KF + H_2\uparrow$

- **Disadvantages of this method :**

(i) Hydrogen and fluorine may get mixed together and may cause explosion.

(ii) Perfectly pure and dry KHF_2 should be used, since the presence of traces of moisture favours the formation of ozonised oxygen.

(iii) The exit tube near the anode being narrow, the liberated fluorine cannot escape sufficiently fast and hence frothing of the electrolyte is produced which further prevents the escape of fluorine.

(3) **Whytlaw— Gray's method :** The essential parts of the electrolytic cell used in this process consist of a rectangular steel vessel wound all around with resistance coil for heating it electrically. It also serves as the cathode. It has an outlet tube at the upper part for the escape of hydrogen gas. The anode is a graphite rod enclosed in a cylinder of monel metal. There is an outlet near the top of the cylinder for the escape of fluorine. The cylinder is perforated at the bottom. It serves as the porous diaphragm separating the anode from the cathode and prevents the mixing of fluorine liberated at the anode with the hydrogen at the cathode. *Teflon* is used for electrical insulation. The electrolyte used is fused potassium hydrogen fluoride. On passing electric current fluorine is evolved at the anode and hydrogen at the cathode. The liberated fluorine passes out through the exit tube of the cylinder and then led into tubes packed with fused NaF which absorbs HF.

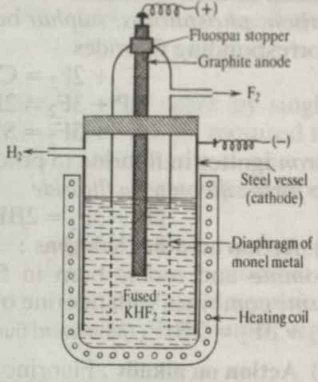


Fig 7.3 : Whytlaw-Gray's method of preparation of F_2

7.3. Properties of fluorine.

[A] **Physical :** (i) Fluorine is a pale greenish yellow gas in thick layers. (ii) It is highly poisonous gas having a pungent and penetrating odour. (iii) It is heavier than air. (iv) It boils at (−181°C) and freezes at (−233°C).

[B] **Chemical :** Fluorine is extremely reactive element. With the exception of oxygen and nitrogen it combines directly with almost all elements.

(i) **Action of hydrogen :** Fluorine has a great affinity for hydrogen. Hydrogen explodes violently with fluorine even in the dark to form hydrogen fluoride.

$$H_2 + F_2 = 2HF$$

(ii) **Action on water :** Fluorine not only attacks free hydrogen but also the hydrogen present in water or other compounds of hydrogen. At ordinary temperature fluorine reacts with water forming hydrofluoric acid liberating ozonised oxygen.

$$2H_2O + 2F_2 = 4HF + O_2 ; \qquad 3H_2O + 3F_2 = 6HF + O_3$$

(iii) **Action on metals :** Almost all metals combine with fluorine producing metallic fluorides.

(a) *Alkali metals* like *sodium, potassium* and *alkaline earth* metals like *calcium*, ignite spontaneously in fluorine at ordinary temperatures yielding the corresponding fluorides.

$$2Na + F_2 = 2NaF ; \qquad 2K + F_2 = 2KF ; \qquad Ca + F_2 = CaF_2$$

(b) *Magnesium, aluminium, silver, nickel, iron* etc. burn in fluorine on gentle heating yielding the corresponding fluorides.

$$2Al + 3F_2 = 2AlF_3 ; \qquad 2Ag + F_2 = 2AgF ; \qquad Mg + F_2 = MgF_2$$

(c) *Gold, platinum, irridium* etc., combine with fluorine at high temperature yielding the respective fluorides.

(d) *Copper* does not appreciably react with fluorine at ordinary or at elevated temperature. This is due to the formation of a protective layer of CuF_2 on the exposed surface of the metal which protects the copper from further attack.

(iv) **Action on non-metals :** (a) *Excepting nitrogen* and *oxygen,* fluorine reacts vigorously with almost all the non-metals even at ordinary temperatures with the formation of their fluorides.

Carbon, phosphorus, sulphur burn in fluorine at ordinary temperatures forming the corresponding fluorides.

$$C + 2F_2 = CF_4 \text{ (carbon tetra fluoride)}$$
$$2P + 3F_2 = 2PF_3 \text{ (phosphorus tri fluoride)}$$
$$S + 3F_2 = SF_6 \text{ (sulphur hexa fluoride)}$$

Boron ignites in fluorine to produce *boron tri fluoride* and *silicon* reacts with the gas to form *silicon tetra fluoride.*

$$2B + 3F_2 = 2BF_3, \qquad Si + 2F_2 = SiF_4$$

(b) **Action on other halogens :**

Bromine and *iodine* burn in fluorine giving rise to the respective fluorides. *Chlorine* combines with fluorine on heating.

$$Br_2 + 3F_2 = 2BrF_3 \text{ (bromine tri fluoride)}, \qquad I_2 + 5F_2 = 2IF_5 \text{ (iodine penta fluoride)}$$

(v) **Action on alkalis :** Fluorine reacts *with dilute solutions of alkalis* giving rise to *oxygen difluoride* and the metal fluoride.

$$2NaOH + 2F_2 = OF_2 + 2NaF + H_2O$$

With concentrated solutions of alkalis, *fluorides* and *oxygen* are formed.

$$4NaOH + 2F_2 = 4NaF + O_2 + 2H_2O$$

(vi) **Displacement reactions :** Fluorine being the most electronegative element, displaces Cl_2, Br_2, I_2 from their compounds.

$$2KCl + F_2 = 2KF + Cl_2\uparrow \qquad 2NaI + F_2 = 2NaF + I_2$$
$$2KBr + F_2 = 2KF + Br_2\uparrow \qquad 2HBr + F_2 = 2HF + Br_2$$

With HBr and HI, *bromine fluoride* and *iodine fluoride* are produced along with bromine and iodine.

$$3F_2 + 4HBr = 4HF + Br_2 + 2BrF$$
$$3F_2 + 4HI = 4HF + I_2 + 2IF$$

It displaces oxygen from silica.

$$SiO_2 + 2F_2 = SiF_4 + O_2$$

(vii) **Reaction with organic compounds :** Fluorine reacts with almost all the organic compounds. Ether, alcohol, terpentine etc., burn spontaneously when they come in contact with fluorine.

(viii) **Oxidising property :** Fluorine being the most electronegative element, has a strong oxidising power. It oxidises *potassium chlorate to potassium per chlorate, potassium sulphate to potassium per sulphate* and *potassium carbonate to potassium per carbonate..*

$$K\overset{+5}{Cl}O_3 + F_2 + H_2O = 2HF + K\overset{+7}{Cl}O_4$$

$$K_2\overset{+4}{C}O_3 + F_2 + H_2O = 2HF + K_2\overset{+6}{C}O_4$$

$$2K_2\overset{+6}{S}O_4 + F_2 = K_2\overset{+7}{S}_2O_8 + 2KF$$

Fluorine can oxidise oxygen to form *oxygen difluoride.* In the formation of this compound oxygen exhibits reducing property. The oxidation number of oxygen in this compound is (+2).

- **Fluorine is the strongest oxidising agent and the most reactive of all the elements—explain why.**

The oxidising power and the reactivity of fluorine can be explained by the following facts—

(i) Fluorine is the most electronegative element. According to Pauling scale its electronegativity is 4. Consequently fluorine atom has a strong tendency to attract electrons from the atoms of other elements. Fluorine thus compels the other elements to combine with it. Due to its strong electronegativity and small size fluorine has a strong tendency to accept electrons from other atoms or ions. As a result, it oxidises all other substances.

(ii) In fluorine molecule the two F-atoms are linked to each other by single covalent bond. The dissociation energy of F—F bond i.e., the energy required to break the F—F bond being minimum, fluorine molecule splits up easily to give off nascent fluorine and this nascent fluorine is extremely active and takes part in all reactions.

(iii) The size of fluorine atom being very small, the electrons of the two atoms which do not take part in forming the covalent bond between the two F-atoms in a fluorine molecule, come very close to each other. As a result a force of repulsion acts between the two atoms. Thus the F—F bond in fluorine molecule becomes very weak.

(iv) The bond energy of fluorine in fluoride compounds is very strong and so it requires a greater amount of energy to break this bond, consequently the tendency to form fluoride compound is much greater.

- **Fluorine is called a 'superhalogen'—explain why.**

Fluorine is the first member of the halogen family whose electronegativity is the highest and the size of the atom is the smallest. Consequently it has a strong tendency to attract electrons from other atoms. The dissociation energy of the F—F bond in fluorine molecule is minimum and so easily splits up to give off nascent fluorine. As a result, it has a super chemical activity for which it reacts with almost all the elements. As a matter of fact fluorine is the most reactive element. For this super chemical reactivity of fluorine, it is called a super halogen.

- **Hydrogen bond in hydrogen fluoride is much stronger than in H_2O, but the b.p. of HF is much lower than that of H_2O—explain why.**

Water is an association of several H_2O molecules by hydrogen bond formation. Consequently liquid water requires additional heat energy to break the attraction due to hydrogen bonding between its molecules. On boiling, all the hydrogen bonds present in liquid water break up and thus the produced steam contains discrete H_2O molecules only. On the other hand hydrofluoric acid $(HF)_n$ does not vapourise as discrete HF molecule on boiling. The vapour of HF contains associated molecules like $(HF)_2$. Thus in the vaporisation of hydrofluoric acid, all the hydrogen bonds do not break. Consequently though hydrogen bonding is stronger and more extensive in HF, it actually requires less heat energy to boil. This is why the boiling point of HF is lower than that of water.

7.4. Uses of fluorine.

(1) In the production of important fluorides, such as, (a) *Uranium hexa fluoride* UF_6 which is used in the separation of U^{235}. (b) *Sulphur hexa fluoride* SF_6 is used as an insulator in high voltage electrical works. (c) *Freon*—a carbon compound of fluorine CF_2Cl_2, is used as a refrigerant. (d) *Sodium fluoride* is used as a disinfectant in the brewing industry for preventing timber rot. (e) *Stannous fluoride* (SnF_2) is used in tooth paste to prevent dental decay. (f) *Boron tri fluoride* is used as a catalyst in the petrolium industry. (g) *Fluoro trichloro methane* CCl_3F is used as insectides. (h) *Teflon* (poly tetra fluoro carbon) is resistant to the action of acids, alkalis and oxidising agents. It is the best insulator used in a low temperature work.

• Comparison of fluorine and oxygen.

Fluorine is the first member of Group VII B, while oxygen is the first member of Group VI B. Fluorine resembles oxygen in some respects due to the following factors—

(i) The atomic and ionic radii of both fluorine and oxygen are very similar.

(ii) Both the elements are highly electronegative.

[A] **Similarities :**

(i) Both oxygen and fluorine are gaseous elements at ordinary temperature. (ii) Both fluorine and oxygen combine with most of the metals and non-metals to produce fluorides and oxides respectively.

$$C + 2F_2 = CF_4 \qquad C + O_2 = CO_2$$
$$Si + 2F_2 = SiF_4 \qquad Si + O_2 = SiO_2$$
$$2Na + F_2 = 2NaF \qquad 4Na + O_2 = 2Na_2O$$

These fluorides and oxides resemble each other in their physical and chemical properties e.g., solubility, volatility, stability, ionic nature etc.

(iii) Both the elements have strong affinity for hydrogen and both of them combine with H_2 to produce HF and H_2O respectively, HF and H_2O resemble each other in the following respects—

(a) Both HF and H_2O possess associated molecules $(HF)_n$ and $(H_2O)_x$ due to hydrogen bonding.

(b) The boiling points of H_2O and HF are abnormally high.

(c) Both HF and H_2O are weak electrolytes and ionising solvents.

(b) Both of them combine with SO_3 or CrO_3 etc.

$$SO_3 + H_2O = H_2SO_4 \text{ or } HSO_3, OH$$
$$2SO_3 + 2HF = 2(HSO_3, F)$$

(e) The heat of formation of both HF and H_2O is similar to each other.

(v) Both fluorine and oxygen combine directly with carbon while the other halogens do not combine with carbon.

(vi) Some elements exhibit higher valencies in their fluorides and oxides, for example the valency of sulphur in SF_6 and SO_3 is 6.

[B] **Dissimilarities :**

(i) Fluorine is more electronegative than oxygen and so fluorine can oxidise oxygen to OF_2.

(ii) Fluorine is more reactive than oxygen. Fluorine reacts with H_2O, NaOH, gold, platinum while oxygen does not react with them.

$$2H_2O + F_2 = 4HF + O_2$$
$$3H_2O + 3F_2 = 6HF + O_3$$

(iii) Oxygen is divalent while fluorine is monovalent.

• Test for fluorine : (i) When a piece of heated glass wool or asbestos cord is introduced into a jar of fluorine, they ignite spontaneously.

(ii) When fluorine is passed through water, a fishy smell is obtained as fluorine attacks water with the evolution of ozonised oxygen.

$$2H_2O + 2F_2 = 4HF + O_2$$
$$3H_2O + 3F_2 = 6HF + O_3$$

• CHLORINE •

Symbol—Cl ; **Atomic NO.—17 ;** **Atomic Weight.—35·5.**
Electronic configuration : $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$; **Oxidation No. : (−1), (+1), (+3), (+5), (+7)**

Chlorine was isolated by Scheele in 1774 and Davy proved its elementary nature. Chlorine is a strong electronegative element and so it is chemically reactive. As a result it does not occur free in nature. It is found in nature mainly in the form of chlorides of sodium, potassium, calcium, magnesium etc. The chief source of chlorine is *common salt* (NaCl). Sea water contains over 3 percent by weight of dissolved chlorides.

7.5. Preparation of chlorine.

1. By the oxidation of hydrochloric acid. :

Laboratory method of preparation of chlorine.

[A] **Principle :** Chlorine is prepared by heating a mixture of *concentrated hydrochloric acid* and *powdered manganese dioxide*. In this reaction manganese dioxide oxidises hydrochloric acid to chlorine. The reaction takes place in two steps. (i) In the first step manganese dioxide reacts with conc. HCl to form a dark brown solution of *manganese trichloride* and evolving chlorine. (ii) In the next step the produced manganese trichloride decomposes on heating with the liberation of chlorine and formation of *manganous chloride*.

$$\begin{array}{c} 2MnO_2 + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O \\ 2MnCl_3 = 2MnCl_2 + Cl_2 \\ \hline 2MnO_2 + 8HCl = 2MnCl_2 + 2Cl_2 + 4H_2O \end{array}$$

$$\text{or, } \overset{+4}{Mn}O_2 + 4H\overset{-1}{Cl} = \overset{+2}{Mn}Cl_2 + \overset{0}{Cl_2} + 2H_2O$$

[B] **Procedure :** (i) Some powdered manganese dioxide is taken in the round bottomed flask fitted with a thistle funnel and a delivery tube. The lower end of the thistle funnel reaches up to the bottom of the flask. (ii) The flask is then clamped to a stand and placed over a wire gauze on a tripod stand. (iii) Conc. hydrochloric acid is poured down the thistle funnel so that the end of the thistle funnel as well as manganese dioxide remain under the acid level. The mixture inside the flask turns deep brown. (iv) The flask is then slowly heated by a burner when greenish yellow chlorine gas along with some vapours of HCl and moisture, is evolved.

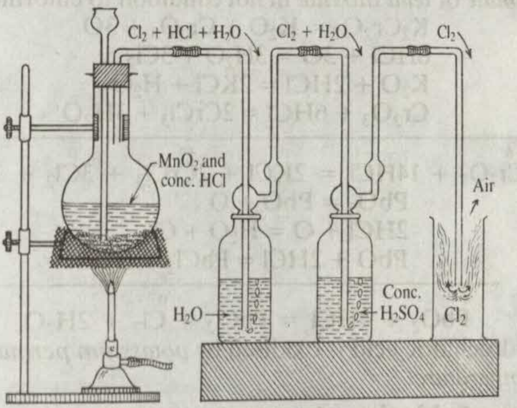


Fig 7.4 : Laboratory method of preparation of Cl_2

[C] **Purification :** (i) The gas coming out of the delivery tube is first passed through a wash bottle containing water. HCl vapour being dissolved in water is removed. (ii) The gas is then passed through another wash bottle containing conc. H_2SO_4 whereby moisture is absorbed.

[D] **Collection :** Chlorine thus freed from moisture and HCl vapour is collected in a gas jar by the upward displacement of air.

[Chlorine is to some extent is soluble in cold water and so it is not collected by the displacement of cold water. Chlorine also attacks mercury. As it is insoluble in aqueous solution of sodium chloride it can be collected by the displacement of NaCl solution.

As chlorine is heavier than air it is usually collected by the upward displacement of air.

When chlorine is passed through water in the wash bottle, it absorbs HCl vapours together with some chlorine. But very soon the water in the wash bottle becomes saturated with chlorine which then passes on without being absorbed in water. HCl vapour being highly soluble in water is absorbed by water.]

2. By heating a mixture of chloride salt, conc. H_2SO_4 and manganese dioxide.

Chlorine may also be prepared in the laboratory by heating a mixture of manganese dioxide, conc. H_2SO_4 and a chloride salt like NaCl, KCl, etc. The reaction takes place in two steps.

(i) In the first step the chloride salt reacts with conc. H_2SO_4 to produce hydrogen chloride.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

(ii) In the second step the produced hydrogen chloride is oxidised by MnO_2 to produce chlorine.

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O$$

This is a general method for the preparation of chlorine bromine and iodine. Bromine and iodine are prepared similarly by using sodium or potassium bromide and iodide respectively.

$$2NaX + 3H_2SO_4 + MnO_2 = 2NaHSO_4 + MnSO_4 + 2H_2O + X_2\ [X = Cl, Br, I]$$

3. By the oxidation of conc. HCl by oxidising agents :

Concentrated hydrochloric acid is oxidised by strong oxidising agents such as *potassium dichromate* or *lead dioxide* in hot condition to chlorine.

$$\begin{array}{c} K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O \\ 6HCl + 3O = 3H_2O + 3Cl_2 \\ K_2O + 2HCl = 2KCl + H_2O \\ Cr_2O_3 + 6HCl = 2CrCl_3 + 3H_2O \\ \hline K_2\overset{+6}{Cr}_2O_7 + 14H\overset{-1}{Cl} = 2KCl + 2\overset{+3}{Cr}Cl_3 + 3\overset{0}{Cl}_2 + 7H_2O \end{array}$$

$$\begin{array}{c} PbO_2 = PbO + O \\ 2HCl + O = H_2O + Cl_2 \\ PbO + 2HCl = PbCl_2 + H_2O \\ \hline \overset{+4}{Pb}O_2 + 4H\overset{-1}{Cl} = \overset{+2}{Pb}Cl_2 + \overset{0}{Cl}_2 + 2H_2O \end{array}$$

Concentrated hydrochloric acid is oxidised by *potassium permanganate to chlorine at an ordinary temperature.*

- **Preparation of chlorine at room temperature :**

Crystals of *potassium permanganate* on treatment with *concentrated hydrochloric acid* yields chlorine at an ordinary temperature. Concentrated hydro chloric acid is oxidised by potassium permanganate to produce chlorine.

$$\begin{array}{c} 2KMnO_4 = K_2O + 2MnO + 5O \\ 10HCl + 5O = 5H_2O + 5Cl_2 \\ K_2O + 2HCl = 2KCl + H_2O \\ 2MnO + 4HCl = 2MnCl_2 + 2H_2O \\ \hline 2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O \end{array}$$

Crystals of potassium permanganate are taken in a conical flask fitted with a dropping funnel and a delivery tube. Cold and concentrated hydrochloric acid is added dropwise from the dropping funnel on the crystals of $KMnO_4$. As soon as the crystals of $KMnO_4$ come in contact with conc. HCl, reaction starts and chlorine is evolved. The evolved chlorine passes out through the delivery tube and is collected in a gas jar by the displacement of air.

If excess hydrochloric acid is added rapidly to the crystals of $KMnO_4$, the reaction becomes vigorous and explosion may take place. So the addition of excess HCl should be avoided.

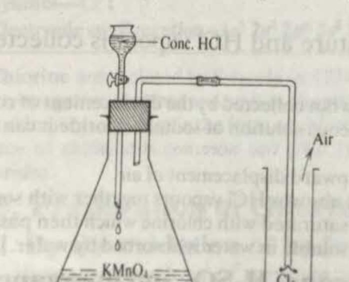
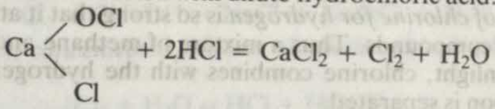


Fig 7.5 : Preparation of Cl_2 at room temperature

4. From bleaching powder :

Chlorine may also be obtained from bleaching powder at ordinary temperature when bleaching powder is reacted with dilute hydrochloric acid.



$$Ca(OCl)Cl + 2HCl = CaCl_2 + Cl_2 + H_2O$$

5. Electrolysis of HCl or fused chlorides :

Electrolysis of conc. HCl or fused NaCl or $SnCl_2$ or AgCl yields chlorine at the anode. These electrolytes are ionised to give Cl^- ions and on passing electric current, Cl^- ions are discharged at the anode to give chlorine.

$$\text{At anode}: Cl^- - e = Cl, \qquad Cl + Cl = Cl_2$$

A pure sample of chlorine is obtained by electrolysing fused silver chloride with carbon electrodes.

7.6. Manufacture of chlorine :

Various types of electrolytic cells are used for the electrolysis of *sodium chloride* solution, *Nelson's cell* is one of such cells. This cell consists of a perforated U-shaped vessel made of steel. This steel vessel is lined inside with porous asbestos. This U-shaped vessel serves as cathode. This vessel is suspended inside a steel tank which is provided with an outlet, a side tube and a tap at the bottom. A saturated solution of sodium chloride (brine) is placed inside the U-shaped vessel. A graphite rod is dipped into the NaCl solution which serves as the anode. On passing electric current the chloride ions move to the anode and are liberated as chlorine gas which escapes through the outlet tube. H^+ ions of water move to the cathode and are liberated as hydrogen. The sodium ions and OH^- ions accumulate in the water in the steel tank by diffusion through the porous asbestos, to form sodium hydroxide. The hydrogen passes out of the tank from an outlet.

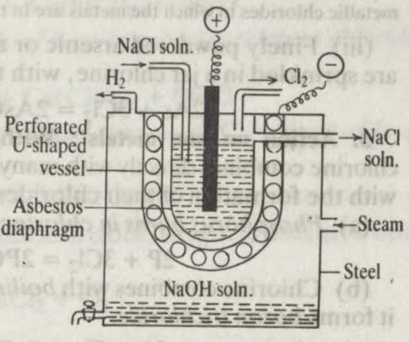


Fig 7.6 : Nelson's cell

$$\begin{array}{llll} \text{Reactions}: & NaCl \rightleftharpoons Na^+ + Cl^- ; & & H_2O \rightleftharpoons H^+ + OH^- \\ \text{At cathode}: & H^+ \; + e & = H & H + H = H_2 \uparrow \\ \text{At anode}: & Cl^- \; - e & = Cl, & Cl + Cl = Cl_2 \uparrow \end{array}$$

7.7. Properties of chlorine.

[A] **Physical :** (i) Chlorine is a greenish yellow gas having a choking and irritating smell. (ii) It is 2·5 times heavier than air. (iii) It is liquefied to a yellow liquid by compressing it at 15°C. (iv) It is sparingly soluble in cold water and insoluble in hot water or in brine. (v) It is poisonous.

[B] **Chemical :** Due to its high electronegativity, chlorine is very reactive element.

1. Action on hydrogen : (i) Chlorine has a great affinity for hydrogen. It has no action on hydrogen in dark but when a mixture of chlorine and hydrogen is kept exposed to sunlight, it explodes violently with the formation of *hydrogen chloride.*

When a jet of hydrogen is ignited in an atmosphere of chlorine, it continues to burn with the formation of hydrogen chloride.

$$H_2 + Cl_2 = 2HCl.$$

(ii) *The affinity of chlorine for hydrogen* is so strong that it attacks the hydrogen present in organic compounds. Thus a mixture of methane and chlorine on being exposed to the sunlight, chlorine combines with the hydrogen of methane with explosion and carbon is separated.

$$CH_4 + 2Cl_2 = C + 4HCl.$$

A filter paper soaked in terpentine ($C_{10}H_{16}$) ignites spontaneously in chlorine with the separation of carbon.

2. Action on metals and metalloids :

(i) Heated *sodium, potassium* and *powdered copper* ignite spontaneously in chlorine with the formation of the corresponding *chlorides.*

$$2Na + Cl_2 = 2NaCl \; ; \qquad Cu + Cl_2 = CuCl_2$$

(ii) Metals like *iron, aluminium, tin, zinc* etc., combine directly with chlorine at high temperature forming their respective *chlorides.*

$$2Fe + 3Cl_2 = 2FeCl_3, \qquad 2Al + 3Cl_2 = 2AlCl_3$$
$$Sn + 2Cl_2 = SnCl_4, \qquad Zn + Cl_2 = ZnCl_2$$

[Metals which exhibit variable valencies, (Cu, Fe, Sn, Hg etc.) on combination with chlorine produce metallic chlorides in which the metals are in their higher valency state.]

(iii) Finely powdered arsenic or antimony catches fire spontaneously when they are sprinkled in a jar chlorine, with the formation of the corresponding chlorides.

$$2As + 3Cl_2 = 2AsCl_3, \qquad 2Sb + 3Cl_2 = 2SbCl_3$$

3. Action on non metals : With the exception of carbon, oxygen, nitrogen, chlorine combines directly with many non-metals like *phosphorus, sulphur, boron* etc. with the formation of their chlorides.

(a) *Phosphorus burns in chlorine* to form *phosphorus tri and pentachlorides.*

$$2P + 3Cl_2 = 2PCl_3, \qquad 2P + 5Cl_2 = 2PCl_5$$

(b) Chlorine combines with *boiling sulphur* to form *sulphur chloride.* With *boron* it forms *boron trichloride.*

$$2S + Cl_2 = S_2Cl_2, \qquad 2B + 3Cl_2 = 2BCl_3$$

4. Action on water : (i) On passing Cl_2 through ice cold water, crystals of different hydrates of chlorine are obtained.

$$Cl_2 + 6H_2O = Cl_2, 6H_2O, \quad Cl_2 + 8H_2O = Cl_2, 8H_2O$$

(ii) Chlorine dissolves in water to form a light yellow solution having a strong smell of chlorine. This is known as chlorine water. Chlorine water contains *hydrochloric acid* and *hypochlorous acid.* These are produced by the action of water on chlorine at ordinary temperature.

$$H_2O + Cl_2 = HCl + HOCl$$

On long standing hypochlorous acid decomposes to give nascent oxygen and HCl.

$$HOCl = HCl + O \uparrow$$

(iii) In presence of *bright sunlight* chlorine reacts with water to form hydrochloric acid and oxygen.

$$Cl_2 + H_2O = 2HCl + O \uparrow$$

5. Action on alkali : (i) Chlorine reacts with *cold* and *dilute solution* of *sodium hydroxide* or *potassium hydroxide* to produce the *chlorides* and *hypochlorites* of sodium or potassium.

$$\begin{array}{c} Cl_2 + H_2O = HCl + HOCl \\ NaOH + HCl = NaCl + H_2O \\ NaOH + HOCl = NaOCl + H_2O \\ \hline \overset{0}{Cl_2} + 2NaOH = Na\overset{-1}{Cl} + NaO\overset{+1}{Cl} + H_2O \end{array}$$

(ii) With *hot and concentrated solution* of *alkalis*, chlorine forms *chlorides* and *chlorates*.

$$\begin{array}{c} [Cl_2 + H_2O = HCl + HOCl] \times 3 \\ [NaOH + HCl = NaCl + H_2O] \times 3 \\ [NaOH + HOCl = NaOCl + H_2O] \times 3 \\ 3NaOCl = NaClO_3 + 2NaCl \\ \hline 6NaOH + 3\overset{0}{Cl_2} = 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O \end{array}$$

(iii) Chlorine reacts with *cold lime water*, i.e., *dilute calcium hydroxide* to produce *calcium chloride* and *calcium hypochlorite*.

$$\begin{array}{c} (Cl_2 + H_2O = HCl + HOCl) \times 2 \\ Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O \\ Ca(OH)_2 + 2HOCl = Ca(OCl)_2 + 2H_2O \\ \hline 2Ca(OH)_2 + 2\overset{0}{Cl_2} = Ca\overset{-1}{Cl_2} + Ca(O\overset{+1}{Cl})_2 + 2H_2O \end{array}$$

(iv) *Excess of chlorine reacts* with *hot milk of lime* to produce *calcium chloride* and *calcium chlorate*.

$$6Cl_2 + 6Ca(OH)_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$

(v) When *dry chlorine* is passed over dry *slaked lime* at 40°C *calcium chloro hypochlorite* (bleaching powder) is obtained.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O$$

(vi) Chlorine on being passed over *red hot calcium oxide, oxygen* is liberated with the formation of calcium chloride.

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2 \uparrow$$

6. Oxidising property : Chlorine is a strong oxidising agent. Its oxidising action is due to the fact that it gives off nascent oxygen in presence of moisture. Chlorine at first reacts with moisture to form HCl and HOCl. HOCl thus produced decomposes to give nascent oxygen.

$$\begin{array}{c} H_2O + Cl_2 = HCl + HOCl \\ HOCl = HCl + O \end{array}$$

(i) Colourless acidified ferrous salts are oxidised to give yellow coloured ferric salts.

$$\begin{array}{c} H_2O + Cl_2 = 2HCl + O \\ 2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O \\ \hline 2\overset{+2}{Fe}SO_4 + Cl_2 + H_2SO_4 = \overset{+3}{Fe_2}(SO_4)_3 + 2HCl \end{array}$$

$$\begin{array}{c} H_2O + Cl_2 = 2HCl + O \\ 2FeCl_2 + 2HCl + O = 2FeCl_3 + H_2O \\ \hline 2FeCl_2 + Cl_2 = 2FeCl_3 \end{array}$$

(ii) *Oxidation of ammonia :*

(a) Chlorine reacts with excess *ammonia* oxidising it to *nitrogen*.

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$
$$6NH_3 + 6HCl = 6NH_4Cl$$
$$8\overset{-3}{N}H_3 + 3Cl_2 = 6NH_4Cl + \overset{0}{N}_2$$

(b) With *excess chlorine*, ammonia is oxidised to *nitrogen trichloride* which is violently explosive liquid.

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl$$

(iii) *Oxidation of hydrogen sulphide* : Hydrogen sulphide is oxidised to sulphur when chlorine is introduced into a jar of hydrogen sulphide or passed through an aqueous solution of H_2S.

$$H_2\overset{-2}{S} + Cl_2 = 2HCl + \overset{0}{S}$$

(iv) *Sulphur dioxide* is oxidised to *sulphuric acid* by chlorine.

$$SO_2 + H_2O = H_2SO_3$$
$$H_2SO_3 + Cl_2 + H_2O = 2HCl + H_2SO_4$$
$$\overset{+4}{S}O_2 + \overset{0}{Cl}_2 + 2H_2O = 2H\overset{-1}{Cl} + H_2\overset{+6}{S}O_4$$

Sodium and potassium sulphites are oxidised to their respective *sulphates*.

$$Na_2\overset{+4}{S}O_3 + Cl_2 + H_2O = 2HCl + Na_2\overset{+6}{S}O_4$$

Chlorine reacts with sodium thiosulphate whereby thiosulphate is oxidised to *sodium sulphate*. This reactions exhibits the difference between chlorine and iodine.

$$Na_2S_2O_3 + 5H_2O + 4Cl_2 = Na_2SO_4 + H_2SO_4 + 8HCl$$

(v) *Bromides* and *iodides* are oxidised to give *bromine* and *iodine* respectively.

$$2KBr + Cl_2 = 2KCl + Br_2, \qquad 2KI + Cl_2 = 2KCl + I_2$$
$$2HBr + Cl_2 = 2HCl + Br_2, \qquad 2HI + Cl_2 = 2HCl + I_2$$

(vi) *Potassium manganate* is oxidised by Cl_2 to *potassium permanganate*.

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$$

(vii) *Potassium ferrocyanide* is oxidised by Cl_2 to give *potassium ferricyanide*.

$$2K_4[Fe(CN)_6] + Cl_2 = 2K_3[Fe(CN)_6] + 2KCl$$

7. Reducing action of chlorine : Chlorine reacts with fluorine and reduces it to *fluorine monochloride* and *fluorine trichloride*. These compounds are called *inter halogen compounds*.

$$\overset{0}{F}_2 + \overset{0}{Cl}_2 = \overset{+1\,-1}{ClF}, \qquad 3\overset{0}{F}_2 + \overset{0}{Cl}_2 = 2\overset{+3\,-1}{ClF_3}$$

8. Formation of addition compounds : *Chlorine combines directly with non-metallic oxides* producing *addition compounds*.

(i) Thus *carbon monoxide* combines with chlorine to form *carbonyl chloride* or *phosgene*.

$$CO + Cl_2 = COCl_2$$

(ii) Chlorine combines with *nitric oxide* to form *nitrosyl chloride* and with *sulphur dioxide* to form *sulphuryl chloride*.

$$2NO + Cl_2 = 2NOCl, \qquad SO_2 + Cl_2 = SO_2Cl_2$$

(iii) Unsaturated organic compounds such as *ethelene, acetylene* etc., form additive compounds with chlorine.

$C_2H_4 + Cl_2 = C_2H_4Cl_2$ *(ethelene dichloride)*
$C_2H_2 + 2Cl_2 = C_2H_2Cl_4$ *(acetylene tetrachloride)*

9. Bleaching property : Dry chlorine has no bleaching property but in presence of moisture, chlorine can bleach vegetable colouring matters. This is due to the fact that during bleaching action, chlorine at first reacts with moisture to produce nascent oxygen and this nascent oxygen bleaches the vegetable colouring matters by oxidation.

$$H_2O + Cl_2 = 2HCl + O$$

$$\text{Vegetable colouring matter} + O \rightarrow \text{colourless product}$$

- **Chlorine cannot bleach the printing ink or the marks of lead pencil—explain why.**

This is because of the fact that printing ink is made of carbon and the lead pencil is made of graphite which is an allotrope of carbon. The marks produced by lead pencil are also graphite. Now chlorine has no action on carbon at ordinary temperature i.e., carbon is not oxidised by the nascent oxygen given off by chlorine by its action on moisture. Consequently printing ink or the marks of a lead pencil are not bleached by chlorine.

- **Moist litmus paper at first turns red and then becomes colourless when it is introduced into a jar of Cl_2—explain why.**

The moist blue litmus paper turns red due to the acidic action of HCl and HOCl, which are produced by the action of chlorine on water.

$$Cl_2 + H_2O = HCl + HOCl.$$

Then the produced HOCl decomposes of give nascent oxygen which oxidises the vegetable colouring matter of the litmus to a colourless product. As a result the red litmus becomes colourless.

$$HOCl = HCl + O$$

$$\begin{array}{c}\text{Vegetable colouring} \\ \text{matter of litmus}\end{array} \xrightarrow{[O]} \text{Colourless product}$$

- **Comparison of the bleaching properties of chlorine with those of sulphur dioxide.**

(i) Both chlorine and sulphur dioxide in dry state cannot bleach dry matters.

(ii) Both chlorine and sulphur dioxide bleach in presence of moisture.

(iii) Chlorine reacts with the moisture liberating nascent oxygen and HCl. This nascent oxygen then oxidises the coloured vegetable matter to produce a colourless product. Thus chlorine bleaches by *oxidation.*

$$H_2O + Cl_2 = 2HCl + O\uparrow$$

$$\text{Coloured vegetable matter} \xrightarrow[\text{oxidation}]{[O]} \text{Colourless product}$$

On the otherhand sulphur dioxide reacts with moisture producing nascent hydrogen and H_2SO_4. This nascent hydrogen then reduces the coloured vegetable matters to produce a colourless product.

$$2H_2O + SO_2 = H_2SO_4 + 2H\uparrow$$

$$\text{Coloured vegetable matter} \xrightarrow[\text{reduction}]{[H]} \text{Colourless product}$$

Thus sulphur dioxide bleaches by *reduction.*

(iv) Chlorine is much stronger bleaching agent than sulphur dioxide and so delicate articles like silk, wool, feathers etc., are damaged when bleached by chlorine. Sulphur dioxide being a mild bleaching agent may safely be used to bleach these delicate articles.

(v) The bleaching action of sulphur dioxide is not permanent. The colour of the original substance is restored on exposure to air, light or on treatment with dilute H_2SO_4. This is due to the fact that as sulphur dioxide bleaches by reduction, the bleached substance is easily oxidised by the oxygen of air to the original substance. But the bleaching action of chlorine is permanent as it bleaches by oxidation and so the bleached substance cannot be oxidised further by the atmospheric oxygen to restore its original colour.

- **Prove that chlorine is an oxidising agent.**

(i) Colourless solution of potassium bromide is taken in a test tube and chlorine gas is passed through it. It is found that the colourless solution turns reddish brown. Now some carbon disulphide is added to this solution and shaken well. After allowing the mixture to stand it is observed that the layer of carbon disulphide turns reddish brown. This proves that chlorine has oxidised KBr to free bromine which dissolves in CS_2 to form the reddish brown layer of CS_2. Thus it is proved that Cl_2 is an oxidising agent.

$$2KBr + Cl_2 = 2KCl + Br_2 \uparrow$$

(ii) A colourless solution of ferrous chloride is taken in a test tube and chlorine gas is passed through it when the solution turns yellow. Now few drops of potassium ferrocyanide are added to this yellow solution when a deep blue precipitate is obtained. This proves the presence of ferric ions in the solution. Thus it is proved that chlorine has oxidised ferrous chloride to ferric chloride.

$$2\overset{+2}{Fe}Cl_2 + Cl_2 = 2\overset{+3}{Fe}Cl_3$$

(iii) Chlorine is passed through an aqueous solution of sulphur dioxide. The resulting solution is then treated with barium chloride solution when a white precipitate is obtained which is found to be insoluble in HCl or HNO_3. Thus it is proved that the white precipitate is barium sulphate which is produced by the action of H_2SO_4 on barium chloride. This H_2SO_4 is obtained by the oxidation of SO_2 by chlorine. Thus it is proved that Cl_2 is an oxidising agent.

$$\overset{+4}{S}O_2 + Cl_2 + 2H_2O = H_2\overset{+6}{S}O_4 + 2HCl$$

- **Dry chlorine cannot bleach, but chlorine in presence of moisture can bleach—explain why.**

Chlorine bleaches by oxidation. In presence of moisture chlorine reacts with water to produce HCl and nascent oxygen. This nascent oxygen oxidises the coloured matters to produce colourless matters.

$$H_2O + Cl_2 = HCl + O$$

$$\text{Coloured matter} + O \rightarrow \text{Colourless matter.}$$

In dry chlorine there is no water. Consequently Cl_2 cannot liberate nascent oxygen to react with the coloured matter. This is why the dry chlorine has no bleaching action.

- **How would you obtain chlorine from potassium chlorate ? Or prove that potassium chlorate contains chlorine.**

A mixture of potassium chlorate and MnO_2 is taken in a hard glass test tube and is heated strongly. Potassium chlorate decomposes to give potassium chloride and oxygen. MnO_2 remains unchanged as it acts as catalyst in this reaction. After the completion of the reaction, the residue left in the test tube is taken in a clean test tube and conc. H_2SO_4 is added to it. The mixture is then heated when a greenish yellow gas having the smell of bleaching powder is found to evolve. When a paper soaked in starch and KI solution is held in the gas, the paper turns blue. This proves that the evolved gas is chlorine.

A mixture of potassium chlorate and MnO_2 on being heated forms potassium chloride with the evolution of O_2.

$$2KClO_3 = 2KCl + 3O_2$$

The residue left in the test tube is a mixture of KCl and MnO_2 which on being heated with conc. H_2SO_4 is oxidised to give chlorine.

$$2KCl + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + Cl_2 + 2H_2O$$

- **Prove that chlorine is a stronger oxidising agent than bromine or iodine.**

A colourless solution of KBr is taken in a test tube and Cl_2 is passed through it. After some time the colourless solution turns reddish brown. This colour is due to the liberation of free bromine in the solution. Thus it is proved that chlorine has displaced bromine from KBr to form KCl and thus KBr is oxidised by Cl_2 to free bromine.

$$2K\overset{-1}{Br} + Cl_2 = 2KCl + \overset{0}{Br_2}$$

When chlorine is passed through a colourless solution of KI, free I_2 is liberated which turns starch solution blue. Thus it is proved that chlorine has oxidised KI to free iodine. These two experiments prove that Cl_2 is stronger oxidising agent than bromine or iodine.

$$2K\overset{-1}{I} + Cl_2 = 2KCl + \overset{0}{I_2}$$

7.8. Test for chlorine.

(i) Chlorine is a greenish yellow gas having the smell of bleaching powder.

(ii) It decolourises moist litmus paper and indigo solution.

(iii) When chlorine is passed through a colourless solution of potassium bromide it turns reddish brown due to the liberation of bromine. To this solution when carbon disulphide is added and shaken then the CS_2 layer turns reddish brown. This is due to fact that chlorine displaces bromine from KBr and the displaced bromine dissolves in CS_2 turning it reddish brown.

$$2KBr + Cl_2 = 2KCl + Br_2$$

(iv) A filter paper soaked in solutions of starch and potassium iodide turns deep blue when it introduced into a jar of chlorine. Chlorine displaces iodine from potassium iodide which produces a deep blue colour with starch.

$$2KI + Cl_2 = 2KCl + I_2$$

$$\text{Starch} + I_2 \rightarrow \text{deep blue colour.}$$

7.9. Uses of chlorine.

(i) It is used as bleaching agent for bleaching linen, cotton, wood pulp etc.

(ii) Chlorine is extensively used in the manufacture of chloro derivatives of organic compounds such as ethyl chloride polyvinyl chloride (plastic P.V.C), chloroform, carbon tetrachloride, D.D.T. etc., which are used as drugs, solvents, anaesthetics, antiseptics, insectides etc.

(iii) It is used in the manufacture of bleaching powder, chlorates, perchlorates, hydrogen chloride, sulphur monochloride, etc.

(iv) It is used to prepare some poisonous gases like phosgene ($COCl_2$), tear gas or chloro picrin, mustard gas [$(C_2H_4Cl)_2S$].

(v) It is used for sterilising drinking water.

- **Similarities and dissimilarities between chlorine and oxygen.**

Oxygen is the first member of Group VI B and Cl_2 is the second member of Group VIIB. Consequently like the elements of other groups of the periodic table, the properties of oxygen resemble more with those of chlorine which is diagonally placed to oxygen in the periodic table, than with members of its own group.

V	VI	VII
N P	O S	F Cl

[A] Similarities :

Property	Oxygen	Chlorine
(i) Physical State	Colourless and odourless gaseous element.	Greenish yellow gaseous element. Having the smell of bleaching powder.
(ii) Oxidising power	Has oxidising power, it can oxidise H_2S, NH_3 etc. $2H_2S + O_2 = 2H_2O + 2S$ $4NH_3 + 3O_2 = 2N_2 + 6H_2O$	Has oxidising power, it can oxidise H_2S, NH_3 etc. $H_2S + Cl_2 = 2HCl + S$ $2NH_3 + 3Cl_2 = N_2 + 6HCl$
(iii) Combination with metals and non-metals	Oxygen forms oxides with metals and non-metals. $4Na + O_2 = 2Na_2O$ $4P + 3O_2 = 2P_2O_3$	Chlorine forms chlorides with metals and non metals. $2Na + Cl_2 = 2NaCl$ $2P + 3Cl_2 = 2PCl_3$
(iv) Action on acids	Oxygen has no action on HNO_3 or H_2SO_4.	Chlorine has no action on HNO_3 and H_2SO_4.
(v) Action on hydrogen	Combines with hydrogen in presence of electric spark to produce water. $2H_2 + O_2 = 2H_2O$	Combines directly with hydrogen in presence of sunlight to form HCl. $H_2 + Cl_2 = 2HCl$

[B] Dissimilarities :

(i) Electronegative character	Oxygen is a strong electronegative element. Its electronegativity is 3.5.	Chlorine is a strong electronegative element. Its electronegativity is 3·0.
(ii) Valency	Oxygen is generally divalent.	Chlorine is mostly monovalent, but it can exhibit valency 4 as well as 7 HCl, ClO_2, Cl_2O_7
(iii) Action on alkalis	Oxygen has no action on alkalis.	Chlorine reacts with alkalis producing chloride, chlorate and hypo chlorite. $2NaOH + Cl_2 = NaCl + NaOCl + H_2O$ $6NaOH + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O$
(iv) Oxidation number	Its oxidation numbers are generally −2 and −1	The oxidation numbers are generally −1, +1, +5, +7
(v) Reactivity	Oxygen is less reactive than Cl_2. It combines with H_2 in presence of electric sparks.	Cl_2 is more reactive than O_2. It combines with H_2 in sunlight.

• BROMINE •

Symbol—Br.	**Atomic No : 35**	**Atomic weight : 79·9**
Electronic configuration :	**[Ar] $3d^{10} 4s^2 4p^5$**	**O.N = −1, +1, +5, +7**

Bromine being an active element, does not occur free in nature. It is found to occur in sea water as bromides of sodium, potassium and magnesium. The mineral *carnallite* contains 0·6 percent of magnesium bromide.

The mother liquor, left after the crystallisation of common salt from sea water is called *bittern* which contains metallic bromides. In 1826 *Balard* first prepared bromine by the action of chlorine on bittern.

7.10. Preparation of bromine.

1. Laboratory method :

[A] **Principle :** In the laboratory bromine is prepared by heating a mixture of *potassium bromide, manganese dioxide* and *concentrated sulphuric acid.* At first hydrobromic acid is produced by the action of conc. H_2SO_4 on KBr, which is subsequently oxidised by MnO_2 to give bromine.

$$\begin{array}{llll}(KBr & + H_2SO_4 & = KHSO_4 & + HBr) \times 2 \\ MnO_2 & + H_2SO_4 & = MnSO_4 & + H_2O + O \\ 2HBr & + O & = H_2O & + Br_2 \\ \hline \end{array}$$

$$2KBr + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + Br_2 + 2H_2O$$

[B] **Procedure :** An intimate mixture of potassium bromide and manganese dioxide is taken in a glass retort and fairly strong sulphuric acid is added to it. The mouth of the retort is then closed with a glass stopper. The retort is then clamped to a stand and placed on the wire gauze on a tripod stand. The open end of the retort is inserted into a round bottomed flask which acts as the receiver. The outside of the receiver flask is kept cooled by flowing cold water.

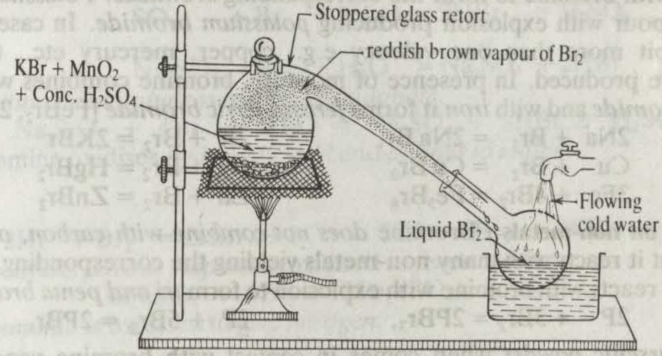


Fig 7.7 : Laboratory method of preparation of bromine

The retort is then heated cautiously when red vapours of bromine are liberated which pass through the long neck of the retort and are condensed to a dark red liquid in the receiving flask.

[C] **Purification :** Bromides always contain traces of chlorides and iodides. So the produced bromine is always contaminated with traces of chlorine and iodine. It is purified by distilling it over a mixture of potassium bromide and zinc oxide. Chlorine is removed by its action on KBr and iodine is removed by its action on zinc oxide. The moisture in bromine is removed by distilling it with concentrated H_2SO_4.

2. By passing chlorine through a staurated solution of potassium bromide.

Bromine can also be prepared in the laboratory by passing *chlorine* through a saturated solution of *potassium bromide* (or *NaBr*). As chlorine is more electronegative than bromine, it displaces bromine from KBr.

$$2KBr + Cl_2 = 2KCl + Br_2$$

The displaced bromine forms a separate layer at the bottom of the reaction vessel. This is separated with the help of a separating funnel.

Bromine may also be obtained by oxidising *bromide salt* by *conc. HNO_3*.

$$6KBr + 8HNO_3 = 6KNO_3 + 2NO + 3Br_2 + 4H_2O$$

7.11. Properties of bromine.

[A] **Physical :** (i) Bromine is a dark red, dense and heavy liquid having a pungent and suffocating odour. *It is the only non metal which is liquid at ordinary temperature.* (ii) Its specific gravity is 3·19 which is greater than that of glass and so a glass stopper floats on liquid bromine. (iii) It is sparingly soluble in water and forms a reddish brown solution in water which is known as bromine water. Bromine is fairly soluble in organic solvents like alcohol, ether, chloroform, carbon disulphide, carbontetra chloride. (iv) It boils at 59°C but produces reddish brown vapours at ordinary temperature. (v) Liquid bromine corrodes skin severely. Bromine vapours attack skin, eyes, nose and throat.

[B] Chemical : Bromine being a member of the halogen family, resembles chlorine in its chemical properties, but it is less reactive than chlorine.

1. Action on metals : *Sodium, potassium, magnesium, copper, mercury* etc., react vigorously with bromine to form the corresponding *bromides. Potassium burns* in bromine vapour with explosion producing *potassium bromide.* In case of metals which exhibit more than one valency e.g., copper, mercury etc., the *higher bromides* are produced. In presence of moisture, bromine combines with *zinc to form zinc bromide* and with *iron* it forms *ferroso ferric bromide* [$FeBr_2$, $2FeBr_3$]

$$\begin{array}{llll} 2Na + Br_2 = 2NaBr, & & 2K + Br_2 = 2KBr \\ Cu + Br_2 = CuBr_2 & & Hg + Br_2 = HgBr_2 \\ 3Fe + 4Br_2 = Fe_3Br_8 & & Zn + Br_2 = ZnBr_2 \end{array}$$

2. Action on non-metals : Bromine *does not combine with carbon, oxygen and nitrogen,* but it reacts with many non-metals yielding the corresponding bromides. *Phosphorus* reacts with bromine with explosion to form *tri and penta bromides.*

$$2P + 3Br_2 = 2PBr_3, \qquad 2P + 5Br_2 = 2PBr_5$$

A little *arsenic powder* when comes in contact with bromine vapour, burns spontaneously with *reddish flame* producing *arsenic tribromide.*

$$2As + 3Br_2 = 2AsBr_3$$

3. Action on hydrogen : Bromine has less affinity for hydrogen than chlorine. It does not combine with hydrogen at ordinary temperature.

On heating bromine vapour with H_2 at 200°C, bromine combines with hydrogen yielding hydrogen bromide.

$$H_2 + Br_2 = 2HBr.$$

4. Action on water : Bromine is sparingly soluble in water and its aqueous solution is called *bromine water.* Bromine water is fairly stable in dark but decomposes in sunlight to give *oxygen and hydro bromic acid.*

$$2H_2O + 2Br_2 = 4HBr + O_2\uparrow$$

When bromine water is cooled to 0°C red crystals of *bromine hydrate* Br_2, $10H_2O$; Br_2, $8H_2O$; separate out.

5. Action on strong alkali :

(a) Bromine reacts with cold and dilute alkali solution of *sodium hydroxide* or *potassium hydroxide* to produce *bromide* and *hypobromite.*

$$\begin{array}{llll} H_2O & + Br_2 & = HBr & + HOBr \\ NaOH & + HBr & = NaBr & + H_2O \\ NaOH & + HOBr & = NaOBr & + H_2O \\ \hline 2NaOH & + Br_2 & = NaBr & + NaOBr + H_2O \end{array}$$

(b) With *hot and concentrated solution* of *alkali,* bromine forms *bromide* and *bromate.*

$$\begin{array}{lllll} (H_2O & + Br_2 & = HBr & + HOBr) & \times 3 \\ (NaOH & + HBr & = NaBr & + H_2O) & \times 3 \\ (NaOH & + HOBr & = NaOBr & + H_2O) & \times 3 \\ 3NaOBr & & = NaBrO_3 & + 2NaBr & \\ \hline 6NaOH & + 3Br_2 & = 5NaBr & + NaBrO_3 + 3H_2O & \end{array}$$

6. Oxidising property. As the electronegativity of bromine is less than that of chlorine, its oxidising power is less than chlorine.

(i) *Hydrogen sulphide* is oxidised to *sulphur* when H_2S is passed through bromine water, bromine itself being reduced to colourless *hydrobromic acid.*

$$H_2\overset{-2}{S} + \overset{0}{Br_2} = 2H\overset{-1}{Br} = \overset{0}{S}\downarrow$$

(ii) Bromine oxidises *sulphur dioxide to sulphuric acid* and *sulphite salts to sulphates.*

$$\overset{+4}{S}O_2 + Br_2 + 2H_2O = 2HBr + H_2\overset{+6}{S}O_4$$

$$Na_2\overset{+4}{S}O_3 + Br_2 + H_2O = Na_2\overset{+6}{S}O_4 + 2HBr$$

(iii) *Sodium thiosulphate* is oxidised to *sulphate.*

$$Na_2S_2O_3 + 4Br_2 + 5H_2O = Na_2SO_4 + 8HBr + H_2SO_4$$

(iv) Bromine oxidises *hydroiodic acid* and *iodides to iodine.*

$$2H\overset{-1}{I} + Br_2 = 2HBr + \overset{0}{I_2}, \qquad 2K\overset{-1}{I} + Br_2 = 2KBr + \overset{0}{I_2}$$

(v) Colourless *ferrous sulphate* is oxidised to *ferric sulphate.*

$$6FeSO_4 + 3Br_2 = 2Fe_2(SO_4)_3 + 2FeBr_3$$

(vi) *Ammonia* is oxidised to give *nitrogen.*

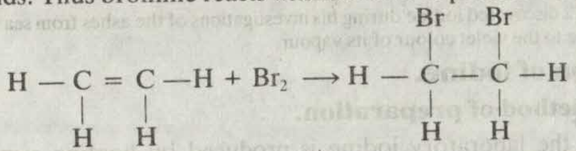
$$8\overset{-3}{N}H_3 + 3Br_2 = 6NH_4Br + \overset{0}{N_2}$$

(vii) *Nitrites* are oxidised to *nitrates.*

$$KNO_2 + Br_2 + H_2O = 2HBr + KNO_3$$

7. Formation of addition compounds.

Bromine combines with *unsaturated organic* compounds to form addition compounds. Thus bromine reacts with *ethelene* to produce *ethelene dibromide.*



$$H-\underset{H}{C}=\underset{H}{C}-H + Br_2 \longrightarrow H-\underset{H}{\overset{Br}{C}}-\underset{H}{\overset{Br}{C}}-H$$

8. Bleaching action : Moist bromine has a *mild bleaching action.* It bleaches vegetable colouring matters by oxidation. It is probable that bromine reacts with water to form HOBr which is responsible for the bleaching action of bromine.

$$H_2O + Br_2 = HOBr + HBr$$

$$HOBr = HBr + O$$

9. Reducing Property—Formation of inter halogen compounds : Bromine exhibits mild reducing property. It reacts with *flourine* and reduces fluorine to *bromine tri* and *penta fluoride.* It also reduces *chlorine* to form *bromine mono chloride.*

$$\overset{0}{Br_2} + 3\overset{0}{F_2} = 2\overset{+3}{Br}\overset{-1}{F_3} \qquad \overset{0}{Br_2} + 5\overset{0}{F_2} = 2\overset{+5}{Br}\overset{-1}{F_5}$$

$$\overset{0}{Br_2} + \overset{0}{Cl_2} = 2\overset{+1}{Br}\overset{-1}{Cl}$$

The compounds formed are called *inter halogen compounds.*

Bromine is absorbed by alkali solution and moist red phosphorus.

- **Tests of bromine :**

(i) Bromine can be identified by its deep red colour and pungent and irritating smell. (ii) It turns starch to orange yellow. (iii) When bromine is shaken with carbon disulphide, bromine dissolves in CS_2 giving a reddish brown solution.

- **Uses of bromine :**

(i) Bromine is used in the preparation of some useful bromides, such as *potassium bromide* (used in medicine), *silver bromide* (used in photography).

(ii) It is also used in the manufacture of *organic dyes, methyl bromide* (a fire extinguisher), *tear gas, ethelene dibromide* which is used in the manufacture of *tetra ethyle lead* (TEL)—*an anti knock compound* in the petrolium industry.

$$\underset{\text{Ethane}}{C_2H_6} + Br_2 = C_2H_5Br + HBr$$

$$4C_2H_5Br + 4Na - Pb = \underset{\text{Tetraethyl lead}}{(C_2H_5)_4Pb} + 4NaBr + 3Pb$$

(iii) It is used in bromination of organic compounds.

• A reddish gas may be NO_2 or Br_2. How would you identify it ?

Bromine vapours and NO_2 are nearly of the same colour. They can be distinguished from each other by the following processes—

(i) Bromine dissolves in CS_2 giving a reddish brown solution while NO_2 does not dissolve in CS_2.

(ii) Bromine dissolves in water giving a reddish brown colour to it while NO_2 dissolves in water giving a colourless solution containing HNO_2 and HNO_3.

• IODINE •

Symbol—I	**Atomic No = 53**	**Atomic weight = 127·92**
Electronic configuration–	**[kr] $4d^{10}\cdot 5s^2 5p^5$**	**Oxidation No.=(−1), (+1), (+5), (+7)**

Iodine is not found in free state in nature. It occurs as metal iodides in sea water, sea weeds and in sea animals. It also occurs as *sodium iodate* with *chili salt peter.*

Barnard courtois, in 1812 discovered iodine during his investigations of the ashes from sea weeds. Gay Lussae named it iodine due to the violet colour of its vapour.

7.12. Preparation of iodine.

1. Laboratory method of preparation.

[A] **Principle** : In the laboratory iodine is produced by heating a mixture of *potassium iodide* (or *NaI*), *manganese dioxide* and *conc.* H_2SO_4. In the first step conc. H_2SO_4 reacts with potassium iodide to produce *hydroiodic acid. In the second stage the produced hydroiodic acid is oxidised by* MnO_2 *to give iodine.*

$$\begin{array}{llllll}
(KI & + H_2SO_4 & = KHSO_4 & + HI)\times 2 & & \\
MnO_2 & + H_2SO_4 & = MnSO_4 & + H_2O & + O & \\
2HI & + O & = H_2O & + I_2 & & \\
\hline
2KI + MnO_2 & + 3H_2SO_4 & = 2KHSO_4 & + MnSO_4 & + 2H_2O & + I_2
\end{array}$$

[B] **Procedure** : An intimate mixture of potassium iodide and manganese dioxide is taken in a glass retort and fairly strong sulphuric acid is added to it. The mouth of the retort is then closed with a glass stopper. The retort is clamped to a stand and placed over a wire gauze on a tripod stand. The open end of the retort is inserted into a round bottomed flask which acts as the receiver. The outside of the receiver is kept cooled by flowing water.

The retort is now carefully heated when violet vapours of iodine are liberated which pass out through the long neck of the retort and are condensed as shining black crystals in the cooler part of the long neck of the retort and in the receiver.

[C] **Purification** : The iodine thus obtained may be contaminated with ICl, IBr and ICN. These are all volatile and consequently it is not possible to separate iodine by sublimation. The I_2 thus obtained is mixed with solid potassium iodide and lime and the mixture heated, when shining black crystals of pure iodine are separated as sublimate. Lime absorbs moisture.

$$ICl + KI = KCl + I_2$$

$$IBr + KI = KBr + I_2$$

[Conc. H_2SO_4 alone can oxidise the HI produced by the action of conc. H_2SO_4 on KI, to iodine.

$$\begin{array}{lllll} (KI & + H_2SO_4 & = KHSO_4 & + HI) \times 2 & \\ & H_2SO_4 & = H_2O & + O + SO_2 & \\ 2HI & + O & = H_2O & + I_2 & \\ \hline 2K\overset{-1}{I} & + 3H_2SO_4 & = 2KHSO_4 & + SO_2 & + \overset{0}{I_2} + 2H_2O \end{array}$$

The addition of MnO_2 only helps the oxidation]

2. Iodine can also be obtained in the laboratory by passing *chlorine* through saturated solution of *potassium iodide* (or NaI). Chlorine being stronger electronegative element than iodine, displaces I_2 from KI.

$$2KI + Cl_2 = 2KCl + I_2$$

Iodine being sparingly soluble in water separates out from the solution. The precipitated iodine is collected by filtration and then sublimated to get pure iodine.

- **Large scale preparation of iodine.**

1. **From Kelp :** The Laminaria variety of sea weeds are collected and burnt in shallow pits to avoid loss of iodine. *The ash of burnt sea weeds is known as kelp.* It contains 0·4–1·3% *iodine* as *iodides*. The kelp is extracted with hot water and the water-extract is concentrated and cooled, when crystals of K_2SO_4, Na_2SO_4, KCl and NaCl separate out. The mother liquor containing iodides, is mixed with manganese dioxide and conc. H_2SO_4 and the mixture is heated in an iron retort. Iodine is liberated which sublimes and condenses in earthen-ware condensers known as *aludels.*

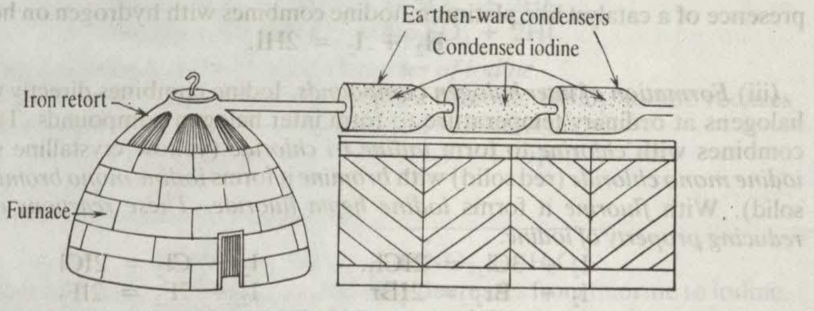


Fig 7.8 : Large scale preparation of iodine

$$\begin{array}{lllll} [NaI & + H_2SO_4 & = NaHSO_4 & + HI] \times 2 & \\ MnO_2 & + H_2SO_4 & = MnSO_4 & + H_2O & + O \\ 2HI & + O & = H_2O & + I_2 & \\ \hline \end{array}$$

$$NaI + 3H_2SO_4 + MnO_2 = 2NaHSO_4 + MnSO_4 + 2H_2O + I_2$$

2. **From chile saltpetre (Caliche) :** *Chile saltpetre* contains about 0·2% *sodium iodate*. It is powdered and dissolved in hot water. The solution is made concentrated and then cooled slowly when crystals of sodium nitrate separate out. The mother liquor containing sodium iodate ($NaIO_3$) is mixed with calculated amount of sodium bisulphite solution when sodium iodate is reduced to iodine. It separates out from the solution as precipitate. It is separated by filtration and is purified by sublimation.

$$2NaIO_3 + 5NaHSO_3 = 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2$$

If $NaHSO_3$ is present in excess it will react with iodine to produce HI.

$$NaHSO_3 + I_2 + H_2O = NaHSO_4 + 2HI$$

7.13. Properties of iodine.

[A] **Physical** : (i) Iodine is a deep brown crystalline solid having shining metallic lustre. (ii) Its specific gravity is 4·9. (iii) It is *sparingly soluble in water* but fairly soluble in *ether, chloroform, carbon disulphide, carbon tetra chloride* etc. The alcoholic solution of iodine is brown while the solutions in CCl_4 or CS_2 is violet. (iv) Solid iodine sublimes on heating to form violet vapours. (v) At above 700°C its diatomic molecules are converted to monoatomic molecules. $I_2 \rightleftharpoons 2I$.

[B] **Chemical** : Iodine resembles chlorine and bromine in many respects but it it less reactive than Cl_2 or Br_2.

1. **Action on non metals :**

(i) *Phosphorus* ignites spontaneously when comes in contact with iodine yielding *phosphorus trichloride*. Burning *arsenic* and *antimony* continue to burn in iodine vapours to form the corresponding *trichlorides*.

$$2P + 3I_2 = 2PI_3$$
$$2As + 3I_2 = 2AsI_3$$
$$2Sb + I_3 = 2SbI_3$$

(ii) *Affinity for hydrogen*—Iodine has much less affinity for hydrogen than that of chlorine or bromine. Even in sunlight it does not combine with hydrogen readily. In presence of a catalyst like platinum, iodine combines with hydrogen on heating.

$$H_2 + I_2 = 2HI.$$

(iii) *Formation of inter halogen compounds.* Iodine combines directly with other halogens at ordinary temperature to form inter halogen compounds. Thus iodine combines with *chlorine* to form *iodine tri chloride* (yellow crystalline solid) and *iodine mono chloride* (red solid) with *bromine* it forms *iodine mono bromide* (black solid). With *fluorine* it forms *iodine hepta fluoride. These reactions exhibit the reducing property of iodine.*

$$I_2 + 3Cl_2 = 2ICl_3, \qquad I_2 + Cl_2 = 2ICl$$
$$I_2 + Br_2 = 2IBr \qquad I_2 + 7F_2 = 2IF_7$$

2. **Action on metals.** (i) *With mercury* : Iodine combines directly with *mercury* at ordinary temperature when a mixture of iodine and mercury is rubbed together. With excess of mercury *green mercurous iodide* is obtained and with excess iodine *red mercuric iodide* is produced.

$$Hg + I_2 = HgI_2, \qquad 2Hg + I_2 = Hg_2I_2$$

(ii) Iodine combines with *sodium, potassium* to form iodides.

$$2Na + I_2 = 2NaI$$

(iii) *Iron* combines with iodine to form *ferrosoferric iodide*, and with *lead* iodine forms *lead iodide.*

$$3Fe + 4I_2 = Fe_3I_8, \qquad Pb + I_2 = PbI_2$$

3. **Action with alkalis :**

(i) With *cold and dilute alkali solutions* such as *sodium hydroxide, potassium hydroxide,* iodine forms *iodides* and *hypoiodites.*

$$2NaOH + I_2 = NaI + NaOI + H_2O.$$

(ii) With *hot and concentrated solutions* of *sodium hydroxide* or *potassium hydroxide,* iodine reacts to form *iodides* and *iodates.*

$$6NaOH + 3I_2 = 5NaI + NaIO_3 + 3H_2O$$

4. **Action on sodium thiosulphate.**

When a colourless solution of *sodium thiosulphate* is added to *iodine suspended in water,* or to a brown solution of *iodine in potassium iodide,* the thiosulphate is oxidised to a colourless solution of *sodium tetrathionate*. The blue colour of the starch-iodine is discharged by this reaction and so this reaction is employed in *iodometry*

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

5. **Formation of additive compounds—reaction with potassium iodide.**

• Iodine is practically insoluble in water but it is highly soluble in aqueous solution of potassium iodide—explain why.

Iodine is sparingly soluble in water, but the crystals of iodine readily dissolve in a colourless solution of potassium iodide turning it brown. This shows that iodine is highly soluble in aqueous solution of potassium iodide. This is because of the fact that *iodine reacts with potassium iodide* to form a *complex salt potassium tri-iodide* which is highly soluble in water. As a result, iodine dissolves in water.

$$KI + I_2 = KI_3$$

6. **Oxidising property :** Iodine is a weak oxidising agent.

(i) It oxidises *hydrogen sulphide* to liberate yellow precipitate of *sulphur*.

$$H_2S + I_2 = 2HI + S\downarrow$$

(ii) Iodine oxidises aqueous solution of *sulphur dioxide* to *sulphuric acid* and a *sulphite* to *sulphate*.

$$\begin{aligned} \overset{+4}{S}O_2 + \overset{0}{I_2} + 2H_2O &= H_2\overset{+6}{S}O_4 + 2H\overset{-1}{I} \\ Na_2SO_3 + I_2 + H_2O &= Na_2SO_4 + 2HI \end{aligned}$$

7. **Reducing property—** *electropositive character of iodine.*

(i) Iodine is the only halogen which is oxidised by conc. HNO_3. Iodine reduces *nitric acid* to *nitrogen dioxide,* itself being oxidised to *iodic acid.*

$$\begin{array}{lll} & (2HNO_3 = H_2O & + 2NO_2 \quad + O)\times 5 \\ I_2 & + 5O & = I_2O_5 \\ I_2O_5 & + H_2O & = 2HIO_3 \\ \hline \overset{0}{I_2} & + 10H\overset{+5}{N}O_3 = 2H\overset{+5}{I}O_3 & + 10\overset{+2}{N}O_2 + 4H_2O \end{array}$$

(ii) The electronegativity of halogens gradually decreases from fluorine to iodine. As a result *iodine though a non-metal, behaves as an electropositive element in some of its compounds.*

$$\overset{0}{I_2} + \overset{0}{Cl_2} = 2\overset{+1}{I}\overset{-1}{Cl}, \qquad \overset{0}{I_2} + 3\overset{0}{Cl_2} = 2\overset{+3}{I}\overset{-1}{Cl_3}$$

8. **Displacement of chlorine and bromine by iodine.**

As the electronegativity of chlorine and bromine is greater than that of iodine, iodine cannot displace chlorine from chlorides and bromine from bromides. But as iodine is more electropositive than chlorine or bromine, it can displace Cl_2 from chlorates and Br_2 from bromates. This is due to the fact that in chlorates and bromates the two halogens are present as electropositive part in the molecules of chlorates and bromates. Consequently being more electropositive element, iodine can replace Cl_2 or Br_2 from chlorates and bromates.

$$\begin{aligned} 2K\overset{+5}{Cl}O_3 + \overset{0}{I_2} &= 2K\overset{+5}{I}O_3 + \overset{0}{Cl_2} \\ 2KBrO_3 + I_2 &= 2KIO_3 + Br_2 \end{aligned}$$

• Iodine is practically insoluble in water while KI is soluble but it is not possible to separate potassium iodide and iodine from a solid mixture of the two by dissolving in water—explain why.

Iodine is practically insoluble in water, but when a solid mixture of iodine and KI is added to water, at first KI dissolves in water forming an aqueous solution of KI. Iodine then reacts with the aqueous solution of KI to form complex salt *potassium tri iodide* which is highly soluble in water. Thus iodine also gets into the solution giving it a brown colour. Thus it is not possible to separate I_2 from KI under the considerations that KI is soluble is water and I_2 is insoluble in it. $KI + I_2 = KI_3$ The mixture may be separated by sublimation when I_2 is obtained as sublimate and KI is left as residue.

- **Iodine and graphite look alike—how would you distinguish them ?**

(i) On heating the two solids separately, iodine sublimes yielding violet vapours. On the other hand graphite at relatively low temperature remains unaffected.

(ii) When a small amount of I_2 is shaken with CS_2, the solution turns violet but when small amount of graphite is shaken with CS_2 it does not dissolve in it.

(iii) Iodine when comes in contact with red phosphorus catches fire forming PI_3, while graphite remains unaffected in red phosphorus.

(iv) Iodine forms a blue complex with starch solution while graphite does not change the colour of the starch solution.

- **To prove that iodine acts as an oxidising agent.**

A fine powder of iodine suspended in water is taken in a conical flask and hydrogen sulphide gas is passed through it. It is observed that the brown colour of the suspended iodine gradually disappears and a colourless solution is obtained together with the precipitation of light yellow substance. The precipitate is collected by filtration. It is washed and dried and then ignited. It is found to burn with a blue flame yielding a colourless gas having the smell of burning sulphur. The evolved gas turns acidified $K_2Cr_2O_7$ solution green. Thus it is proved that the gas is SO_2 which is produced by the burning of the yellow precipitate. So the yellow precipitate is sulphur which is obtained by the oxidation of H_2S by iodine.

$$H_2S + I_2 = 2HI + S\downarrow$$
$$S + O_2 = SO_2$$

- **Illustrate the reducing property of iodine.**

Some crystals of iodine are taken in a test tube and conc. HNO_3 is added to it. The mixture is then boiled. It is observed that the brown colour of iodine gradually disappears and a colourless solution is obtained with the evolution of a colourless gas. It is further observed that as soon as the colourless gas comes out of the test tube and comes in contact with air, turns brown. Thus it is proved that the colourless gas is nitric oxide which is obtained by the reduction of nitric acid.

$$3\overset{0}{I_2} + 10H\overset{+5}{N}O_3 = 6H\overset{+5}{I}O_3 + 10\overset{+2}{N}O + 2H_2O$$
$$2NO + O_2\,(\text{air}) = 2NO_2\,(\text{brown})$$

- **The brown colour of an acidified dilute solution of iodine in aqueous KI solution is intensified by the addition of a nitrite, but is discharged by the addition of a sulphite—Explain why.**

When nitrite salt is added to an acidified solution of iodine in aqueous KI solution, nitrous acid is produced by the action of acid on the nitrite. The produced HNO_2 oxidises KI to form iodine and so the brown colour of the solution. becomes intensified.

$$NaNO_2 + HCl = HNO_2 + NaCl$$
$$2KI + 2HNO_2 = I_2 + 2KOH + 2NO$$

On the other hand if sulphite is added to above solution, sulphurous acid is produced by the action of sulphite on the acid. H_2SO_3 thus produced reduces I_2 of the solution to colourless HI. As a result the solution becomes colourless.

$$Na_2SO_3 + 2HCl = 2NaCl + H_2SO_3$$
$$I_2 + H_2SO_3 + H_2O = H_2SO_4 + 2HI$$

7.14. Tests of iodine.

(i) When crystals of iodine are dropped in a hot flask, violet vapours of iodine are produced.

(ii) Iodine dissolves in CS_2 or CCl_4 producing a violet solution.

(iii) It turns starch solution deep blue.

(iv) When iodine is warmed with ethyl alcohol and caustic soda, it dissolves to form a solution which on cooling yields yellow *crystals of iodoform* having a characteristic smell.

$$
\begin{array}{llll}
CH_3CH_2OH & +I_2 & \rightarrow CH_3CHO & +2HI \\
CH_3CHO & +3I_2 & \rightarrow CI_3CHO & +3HI \\
CI_3CHO & +NaOH & \rightarrow CHI_3 & +HCOONa \\
5HI & +5NaOH & \rightarrow 5NaI & +5H_2O \\
\hline
CH_3CH_2OH + 4I_2 & +6NaOH & \rightarrow 5NaI & +HCOONa + CHI_3 + 5H_2O
\end{array}
$$

7.15. Uses of iodine.

(i) Iodine is used to prepare iodoform, tincture iodine which are used as antiseptic in dressing wounds.

(ii) It is used in the preparation of certain dyes, potassium iodide.

(iii) It is used in the volumetric analysis and as a catalyst. It is also used as mild oxidising agent.

- **Position of halogens in the periodic table :**

Fluorine, chlorine, bromine and iodine belong to the halogen family and have been placed in group VII B in the periodic table. These elements show a marked resemblance in chemical properties and exhibit a well marked gradation in their physical and chemical properties with the increase of atomic number. The inclusion of the halogens in the same group (VIIB) is justified by the following points—

1. **Physical properties.**

The gradation in the physical properties of halogens are tabulated below.

Physical property	Fluorine	Chlorine	Bromine	Iodine
1. Physical state, colour and odour	Pale greenish yellow gas having a pungent and irritating smell.	Greenish yellow gas with an irritating smell	Deep red liquid with an extremely irritating smell	Dark grey crystalline solid with metallic lustre
2. Atomic weight	19	35·457	79·916	126·93
3. Atomic number	9	17	35	53
4. Melting point	—233°C	—102·4°C	—7·2°C	113·6°C
5. Specific gravity	Slightly heavier than air	2½ times heavier than air	Sp.gr=3·19	Sp.gr=4·94
6. Solubility	Decomposes water	Fairly soluble in water	less soluble than Cl_2	Almost insoluble in water.
7. Electronegativity Pauling scale	4	3	2·8	2·5
8. Atomic radius	0·72Å	0·99Å	1·14Å	1·33Å

Thus from the above table it is clear that (i) the density, melting point, atomic radius of the halogens gradually increase with the increase of their atomic numbers.

(ii) The *solubility* and *electronegativity gradually decrease* with the increase of atomic members.

(iii) **Ionisation potentials :** The ionisation potentials of the halogens are very high. These values gradually decrease from fluorine to iodine. Due to its lowest ionisation potential and large size of atom, iodine has a tendency to lose an electron to form I^+ ion. As a matter of fact due to its low value of ionisation potential, iodine exhibits basic character.

(iv) **Oxidation states :** All the halogens have seven electrons ($ns^2\ np^5$) in the outer most orbit. Fluorine being most electronegative exhibits -1 oxidation state only but the other halogens (Cl, Br, I) exhibit variable oxidation states both positive and negative. The possible oxidation states of chlorine are −1, +1, +3, +5 and +7, of bromine are −1, +1, +3, +4 and +6 and of iodine are −1, +1, +3, +5 and +7.

(v) The stability of diatomic molecules towards heat, decreases from chlorine to iodine.

(vi) **Electron affinity :** The electron affinity of halogens decreases from chlorine to iodine. *However fluorine has the lowest electron affinity.* This is due to its small size with high electron density. Consequently a force of repulsion acts between the electron added and the electrons which are already present in the atom.

2. **Similarities in chemical properties and gradation in them.**

(i) The electronic configurations of the halogen atoms are given below :

Element	Atomic No.	Electronic configuration	Valence shell configuration
Fluorine	9	2,7	$2s^2\ 2p^5$
Chlorine	17	2,8,7	$3s^2\ 3p^5$
Bromine	35	2,8,18,7	$4s^2\ 4p^5$
Iodine	53	2,8,18,18,7	$5s^2\ 5p^5$

The identical electronic configuration of the valence shell accounts for the resemblance in their chemical behavior.

(ii) **Occurrence :** Being extremely chemically active, the halogens do not occur free in nature. Each of them is non metal.

(iii) **Preparation :** With the exception of fluorine, the other three (Chlorine, bromine and iodine) are prepared by similar process from the metallic halides.

$$2NaX + MnO_2 + 3H_2SO_4 = 2NaH\,SO_4 + MnSO_4 + X_2 + 2H_2O$$

$$(X = Cl, Br, I)$$

(iv) **Reaction with hydrogen :** The affinity for hydrogen decreases from F_2 to I_2. Fluorine combines with hydrogen with explosive violence even in the dark and at a low temperature. Chlorine combines with H_2 on exposure to sunlight. Bromine reacts with hydrogen on heating and iodine unites with H_2 partially on heating in presence of a catalyst. The stablity of hydrogen halides decreases from HF to HI.

(v) **Stability :** Halogens are diatomic molecules. The stability of the covalent bond decreases as the size of the atom increases. This is because of the fact that the larger atoms can not exert a greater force of attraction on the electron pair which holds the two atoms together. Consequently a halogen molecule having larger atomic size should have low dissociation energy and vice-versa. This holds good for Cl_2, Br_2 and I_2 leaving fluorine as exception. The thermal stability of halogen molecules decreases from Cl_2 to I_2. Dissociation does not occur in case of fluorine. Chlorine dissociates a little above 1100°C, while bromine dissociates only 6% and iodine dissociates to a large extent above 1100°C.

(vi) **Action on water :** Fluorine being the most reactive of all halogens decomposes water at ordinary temperature with the formation of hydrogen fluoride and ozonised oxygen.

$$2H_2O + 2F_2 = 4HF + O_2, \qquad 3H_2O + 3F_2 = 6HF + O_3$$

Chlorine reacts with water in bright sunlight to form HCl and O_2, while bromine reacts with water slowly in bright sunlight.

$$X_2 + H_2O = HX + HOX$$

$$2HOX = 2HX + O_2 \qquad (X = Cl, Br)$$

Iodine does not react with water.

(vii) **Action on alkalis :** Fluorine decomposes dilute alkali producing *oxygen difluoride* and NaF. It reacts with concentrated alkali yielding O_2 and NaF.

$$2F_2 + 2NaOH\,(\text{dil.}) = 2NaF + OF_2 + H_2O$$
$$2F_2 + 4NaOH\,(\text{conc.}) = 4NaF + O_2 + 2H_2O$$

With cold and dilute alkali chlorine produces *chlorides* and *hypochlorites* and with hot and concentrated solution gives *chloride* and *chlorate*. Under identical conditions bromine and iodine form similar salts.

$$2NaOH + X_2 = NaX + NaOX + H_2O$$
$$6NaOH + 3X_2 = 5NaX + NaXO_3 + 3H_2O$$
$$(X = Cl, Br, I)$$

(viii) **Reactions with metals :** Fluorine attacks almost all metals. Au and Pt react with fluorine on heating. Chlorine also attacks almost all metals. Bromine attacks many metals and iodine combines with a few metals. The action of halogens with the metals decreases from fluorine to iodine.

(ix) **Action on non metals :** Fluorine combines violently with almost all non metals with the exception of O_2 and N_2. Chlorine combines directly with almost all the non metals except O_2, N_2 and C. Bromine does not react with O_2, N_2, C and Si. Iodine can combine only with P, As, Sb, H_2 and with halogens.

(x) **Reactivity—displacement of halogens from halides :** Of all the halogens, fluorine is the most reactive due to its small size, high electronegativity, low dissociation energy of F−F bond. The reactivity decreases remarkably from F_2 to I_2. Thus in the displacement reactions, fluorine displaces the other halogens from their salts.

$$2KCl + F_2 = 2KF + Cl_2 \qquad 2KBr + F_2 = 2KF + Br_2$$

Chlorine can displace bromine and iodine from their salts.

$$2KBr + Cl_2 = 2KCl + Br_2 \qquad 2KI + Cl_2 = 2KCl + I_2$$

Bromine displaces only iodine while iodine displaces none of the halogens from their salts.

(xi) **Oxidising power :** The oxidising power of the halogens decreases from fluorine to iodine. The oxidising power of iodine is the least, on the other hand it exhibits reducing property.

(xii) **Bleaching property :** The bleaching property of halogens depends on their oxidising power. Thus fluorine decomposes the colouring matters. The bleaching property decreases from chlorine to bromine. Iodine has no bleaching property.

(xiii) **Formation of oxides :** The halogens do not combine directly with oxygen but they combine with oxygen indirectly to form a number of halogen oxides. These are given below—

Halogens	**Oxides of halogens**
Fluorine	OF_2, O_2F_2
Chlorine	Cl_2O, ClO_2, Cl_2O_6, Cl_2O_7
Bromine	Br_2O, BrO_2, BrO_3
Iodine	I_2O_5

Thus it is found that chlorine forms a greater number of oxides while iodine gives the least. Due to the small difference in the electronegativity between oxygen and the halogens, they are linked to oxygen mainly by covalent bonds. *As fluorine is more electronegative than oxygen, its compounds with oxygen should be called fluorides of oxygen instead of oxides of fluorine.*

(xiv) **Oxyacids :** *Fluorine does not form any oxyacid as it is more electronegative than oxygen.* Oxyacids formed by chlorine, bromine and iodine are classified into 4 types. (a) Hypohalous acids (HOX), (b) Halous acids (HXO_2), (c) Halic acids

(HXO_3) and Perhalic acids (HXO_4). *The strength of these acids increases with the increase of the oxidation states of the halogen atom present in the acid. Thus the acidic nature and stability of the oxyacids of chlorine are in order—*

$$HOCl < HClO_2 < HClO_3 < HClO_4$$

(xv) **Formation of inter halogen compounds :** The halogens combine with one another to produce a number of covalent compounds known as *inter halogen compounds*. The inter halogen compounds are of 4 types—AX, AX_3, AX_5 and AX_7

Type	Chlorine	Bromine	Iodine
AX	ClF	BrF, BrCl	ICl, IBr
AX_3	ClF_3	BrF_3	ICl_3
AX_5		BrF_5	IF_5
AX_7			IF_7

- **Some properties of halogens in the increasing order—**

(i)	Electronegativity	$I < Br < Cl < F$
(ii)	Ionisation potential	$I < Br < Cl < F$
(iii)	Oxidising power	$I < Br < Cl < F$
(iv)	Affinity for H_2	$I < Br < Cl < F$
(v)	Stability as diatomic molecule	$I < Br < Cl < F$
(vi)	Chemical reactivity	$I < Br < Cl < F$
(vii)	Boiling point	$F < Cl < Br < I$
(viii)	Density	$F < Cl < Br < I$

- **Comparison of the chemical properties of halogens :**

Properties	Fluorine	Chlorine	Bromine	Iodine
(i) Affinity for H_2	Combines with explosion even in dark to form HF	Combines in presence of light to form HCl	Combines on heating to form HBr	Combines on heating in presence of a catalyst to form HI
(ii) Action on water	Decomposes water to form HF and ozonised oxygen	Forms chlorine hydrate with ice cold water. Slowly decomposes water at ordinary temperature forming HCl and O_2	Slightly soluble in water and decomposes in sun light to form HBr and O_2	Practically insoluble in water
(iii) Chemical reactivity	Highly reactive	Quite reactive	Less reactive	Less reactive than Br_2
(iv) Displacement of halides by other halogens	Displaces Cl_2, Br_2 and I_2 from their salts	Displaces Br_2 and I_2 from their salts	Displaces I_2 from iodides	Can not displace any halogen
(v) Action on alkalis	With cold and dilute alkalis forms fluorides and F_2O. With conc. alkalis gives fluorides and O_2	With cold and dil. alkalis gives chlorides and hypochlorites. With conc. alkalis give chlorides and chlorates	With cold and dil. alkalis gives bromides and hypobromites. With conc. alkalis give bromides and bromates	With dilute alkalis gives iodides and hypoiodites. With conc. alkalis give iodides and iodates

Properties	Fluorine	Chlorine	Bromine	Iodine
(vi) Oxidising power	Very strong oxidising agent	Strong oxidising agent	Mild oxidising agent	Has feeble oxidising power
(vii) Bleaching action	Highly active, destroys vegetable colouring matters	Bleaches vegetable colours with ease	Has mild bleaching power	Has no bleaching action
(viii) Action on starch solution	No change of colour	No change of colour	Turns yellow	Turns deep blue
(ix) Action on oxidising agent (O_2)	Can not be oxidised—on the other hand it oxidises O_2 to F_2O and F_2O_2	Indirectly oxidised to form Cl_2O, ClO_2, Cl_2O_7 etc.	Indirectly oxidised to form BrO_2, Br_2O	Oxidised by conc. HNO_3, O_2 etc.
(x) Oxidation state	Only −1 in all compounds	−1, +1, +3, +5 and +7 in different compounds	−1, +1, +3 and +5 in different compounds	−1, +1, +3, +5 and +7
(xi) Action on non-metals	With the exception of N_2 and O_2 it combines with all non metals	With the exception of C, N_2, O_2 it combines with many non metals	Combines with many non-metals except C, N_2, O_2 and Si	Combines only with P and As directly
(xii) Action on metals	Reacts with all metals to form fluorides	Reacts with many metals forming chlorides	Reacts with many metals to form bromides	Reacts with few metals

Hydracids of halogens

All the members of the halogen family (F, Cl, Br, I) combine with hydrogen by covalent bond to form volatile hydrogen halides HX (X = F, Cl, Br, I). The oxidation state of each of the halogens in these hydrides is (−1). These hydrides are known as *halogen acids or hydracids of halogens*. There are four hydracids of halogens.

(i) **Hydrogen fluoride (HF)**, (ii) **Hydrogen chloride (HCl)**, (iii) **Hydrogen bromide (HBr)**, (iv) **Hydrogen iodide (HI)**.

• HYDROGEN FLUORIDE (HF) •

7.16. Preparation of hydrogen fluoride.

Fluorine combines with hydrogen directly to form hydrogen fluoride. The reaction is so vigorous that explosion takes place even in the dark. Consequently hydrogen fluoride cannot be prepared by the direct combination of fluorine and hydrogen. An aqueous solution of hydrogen fluoride is prepared by the following process.

1. Preparation of hydrogen fluoride from fluorspar.

[A] **Principle** : Hydrogen fluoride is prepared by distilling *a mixture of powdered fluorspar and 90% sulphuric acid*—the mixture being cautiously heated below 300°C on a sand bath.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF\uparrow$$

[B] Procedure : Powdered fluorspar is taken in a lead retort and 90% conc. H_2SO_4 is added to it. The mixture is then heated on a sand bath below 300°C (as the m.p. of lead is 327°C). Reaction takes place and vapours of hydrogen fluoride are evolved. The evolved hydrogen fluoride vapours are absorbed in water contained in a lead receiver. The hydrogen fluoride gas being dissolved in water forms hydrofluoric acid.

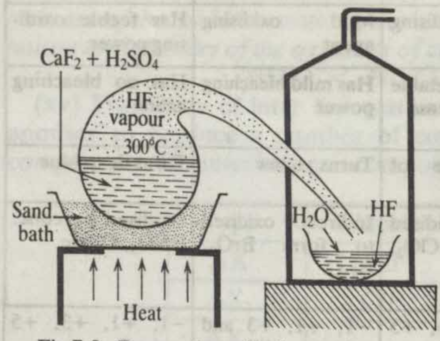


Fig 7.9 : Preparation of hydrogen fluoride

- **Hydrofluoric acid or hydrogen fluoride can not be prepared or stored in a glass or porcelain vessel—explain why.**

Hydrofluoric acid attacks glass or porcelain. When HF is kept is a glass or porcelain vessel, it reacts with silica which is one of the constituents of glass or porcelain forming SiF_4 and H_2SiF_6. For this reason HF can not be kept in bottles made of glass or porcelain. For the same reason HF can not be prepared in apparatus made of glass or porcelain.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$
$$SiF_4 + 2HF = H_2SiF_6$$

Hydrofluoric acid may be stored in *gutta purcha or polythene or wax coated bottle.*

2. Preparation of anhydrous hydrogen fluoride :

[A] Anhydrous hydrogen fluoride is generally prepared by heating *potassium hydrogen fluoride or Fremy's salt,* when potassium hydrogen fluoride is thermally decomposed to yield anhydrous hydrogen fluoride.

$$KHF_2 = KF + HF\uparrow$$

[B] **Procedure :** Dry potassium hydrogen fluoride is taken in a platinum or copper retort which is connected with a condenser made of the same metal. It is kept immersed in a freezing mixture. At first the retort is heated gently to drive off any moisture and then strongly to cause the thermal decomposition of KHF_2. Anhydrous hydrogen fluoride distills over and is collected in a platinum or copper receiver surrounded by freezing mixture. (Pure HF does not attack copper).

Traces of *moisture* which may remain are removed from HF, by *electrolying between platinum electrodes.* The acid stops conducting electricity when it becomes freed from water (as anhydrous HF is a non conductor of electricity).

Fremy's Salt : Equal volumes of an aqueous solution of hydrofluoric acid is taken in two different beakers. One portion of the acid solution is neutralised by adding potassium carbonate. The acid being thus neutralised, the other portion of the HF solution is added to this neutral liquid and the solution thus obtained is evaporated to dryness on a platinum dish. Fremy's salt is obtained as *white crystals.*

$$2HF + K_2CO_3 = 2KF + CO_2 + H_2O \; ; \qquad KF + HF = KHF_2$$

7.17. Properties of hydrofluoric acid.

[A] **Physical :** (i) Anhydrous hydrogen fluoride is a colourless fuming liquid below 19·5°C. Above 19·5°C it is a colourless gas. (ii) It is highly soluble in water. (iii) Anhydrous hydrofluoric acid is a non-conductor of electricity but its aqueous solution conducts electricity. (iv) It is highly poisonous and causes painful wounds on skin.

[B] Chemical

1. Acid property :

- ***HF though a monobasic acid it can form acid salt.***

In aqueous solution, hydrofluoric acid ionises giving H^+ and F^- ions. Thus it gives one H^+ ion per molecule and consequently it should behave as a *monobasic* acid.

$$HF \rightleftharpoons H^+ + F^-$$

The F^- ion thus produced, forms hydrogen bond with an undissociated hydrogen fluoride molecule to form HF_2^- ion.

$$F^- + HF \rightleftharpoons HF_2^-$$

As a result, though hydrofluoric acid is a monobasic acid i.e., inspite of the presence of a single hydrogen atom in its molecule, hydrofluoric acid forms acid salts like potassium hydrogen fluoride or sodium hydrogen fluoride.

$$\begin{aligned} H_2F_2 &+ KOH &= KHF_2 &+ H_2O \\ H_2F_2 &+ NaOH &= NaHF_2 &+ H_2O \end{aligned}$$

• HF has higher boiling point than HCl and it behaves as a weak acid. —explain why.

Liquid hydrogen fluoride consists of associated molecules. In liquid state, HF molecules are associated by hydrogen bonding. Electron diffraction experiments goes to prove that HF consists of polymers of zigzag chains joined by hydrogen bonds, the H−F---H bond angle being 140°. Due to the presence of hydrogen bonding between its molecules, HF is a liquid while hydrogen chloride is a gas inspite of having higher molecular weight than HF.

In aqueous solution, hydrofluoric acid ionises as $HF \rightleftharpoons H^+ + F^-$. The F^- ion thus produced combines with undissociated HF molecule by hydrogen bond to form HF_2^- ion.

$$F^- + HF \rightleftharpoons HF_2^-$$

For the first reaction the ionisation constant $K_1 = \dfrac{[H^+][F^-]}{[HF]} = 7{\cdot}2 \times 10^{-4}$

and that of the second reaction $K_2 = \dfrac{[HF_2^-]}{[F^-][HF]} = 5{\cdot}5$

The strength of acid increases with the increasing value of *K*. Thus it is proved that HF is very weak but HF_2^- is a strong acid.

(a) **Action on metals :** The aqueous solution of hydrofluoric acid attacks all but the noble metals yielding *fluorides and hydrogen.* Anhydrous acid does not attack metals except potassium.

$$\begin{aligned} 2Na + 2HF &= 2NaF + H_2\,; &\quad 2Ag + 2HF &= 2AgF + H_2 \\ NaF + HF &= NaHF_2\,; &\quad Fe + 2HF &= FeF_2 + H_2 \end{aligned}$$

(b) **Action on carbonates :** An aqueous solution of hydrofluoric acid reacts with *carbonates* forming *fluorides* with the evolution of CO_2.

$$Na_2CO_3 + 2HF = 2NaF + CO_2 + H_2O$$

2. **Action on glass (silica) :** Hydrofluoric acid reacts with silica yielding volatile and colourless *silicon tetrafluoride.* This compound further reacts with HF to form *hydrofluo silicic acid.*

$$\begin{aligned} SiO_2 &+ 4HF = SiF_4 + 2H_2O \\ SiF_4 &+ 2HF = H_2SiF_6 \end{aligned}$$

Since glass contains silica which is attacked by hydrofluoric acid, it can not be kept in glass vessel. Hydrofluoric acid is kept in containers made of *gutta-percha, polythene* or *glass bottles having a layer of wax* inside the bottle. Glass consists of SiO_2, Na_2SiO_3, $CaSiO_3$ etc. Hydrofluoric acid reacts with these compounds forming SiF_4, H_2SiF_6 and its salts.

(i) *With SiO_2 :* $SiO_2 + 4HF = SiF_4 + 2H_2O$

$SiF_4 + 2HF = H_2SiF_6$

(ii) *With Na_2SiO_3 :* $Na_2SiO_3 + 2HF = 2NaF + H_2O + SiO_2$

$SiO_2 + 4HF = SiF_4 + 2H_2O$

$2NaF + SiF_4 = Na_2SiF_6$

(iii) *With $CaSiO_3$:* $CaSiO_3 + 6HF = CaSiF_6 + 3H_2O$

The etching of glass is based on the above reactions.

3. **Stability :** Hydrofluoric acid is extremely stable as the H−F bond is very strong. It can not be oxidised even by the strongest oxidising agents. It is not decomposed by heat.

4. **Action on silver nitrate :** On being treated with silver nitrate solution, *it gives no precipitate* since *silver fluoride is soluble* in water *(other silver halides are insoluble in water).*

$$AgNO_3 + HF = AgF + HNO_3$$

5. **With barium chloride :** It reacts with barium chloride solution to form *barium fluoride* which is insoluble and as a result a white precipitate is obtained. *BaF_2 is insoluble in HNO_3 but soluble in conc. HCl (difference from other halogen acids).*

$$BaCl_2 + 2HF = BaF_2\downarrow + 2HCl$$

6. **Formation of complex acids :** Hydrofluoric acid reacts with *boric acid* or *boron trifluoride* to form complex acid *fluo boric acid* (HBF_4) and with *silicon tetrafluoride* to form *hydrofluo silicic acid.*

$$BF_3 + HF = HBF_4$$
$$H_3BO_3 + 4HF = HBF_4 + 3H_2O$$
$$SiF_4 + 2HF = H_2SiF_6$$

7.18. Tests of HF and fluorides.

(i) Hydrofluoric acid is detected by its etching of glass.

(ii) Finely powdered fluoride is treated with conc. H_2SO_4 in a test tube and the mixture is heated when fumes of SiF_4 are evolved. Now a water drop suspended from a glass rod on exposure to the fumes becomes opaque due to the formation of a thin waxy layer of H_2SiO_4 around the water drop.

Conc. H_2SO_4 reacts with the fluoride salt to form HF, which reacts with the silica present in the glass to form the fumes of SiF_4. The produced SiF_4 reacts with water to form white gelatinous silicic acid and as a result the transparent water drop turns opaque.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF\ ; \qquad SiO_2 + 4HF = SiF_4 + 2H_2O$$
$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4 \text{ (ortho silicic acid)}$$

In case of testing free hydrofluoric acid, conc. H_2SO_4 is not added.

(iii) To the solution of a fluoride or hydrofluoric acid, barium chloride solution is added, when a white precipitate of barium fluoride is obtained . The precipitate is insoluble in HNO_3 but soluble is conc. HCl.

$$CaF_2 + BaCl_2 = BaF_2\downarrow + CaCl_2$$

7.19. Uses of hydrogen fluoride.

(i) Hydrofluoric acid is used for *etching glass.* The glass article is first coated with a thin layer of wax. The design is then drawn on the layer of wax with a needle to remove the wax. The surface is then treated with an aqueous solution of HF or exposed to vapours of HF in a lead vessel. The article is then washed with terpentine to remove the wax.

(ii) It is used in the manufacture of plastics like *teflon* and *Kel-F* which are extensively used for their chemical inertness and high thermal stability.

(iii) It is extensively used for removing silica from artificial graphite or iron castings.

(iv) It is used in the preparation of *artificial cryolite* ($Na_3\ AlF_6$) and AlF_3 both of which are used in the metallurgy of aluminium.

(v) Anhydrous HF in liquid state is used as catalyst in the petrolium industry.

(vi) HF is used in the preparation of uranium hexafluoride (UF_6) which is employed for the separation of uranium isotopes.

(vii) Stannous fluoride is used as a constituent of tooth pastes.

• **Fluorides :** *The salts of hydrofluoric acid are known as fluorides.* Many properties of these salts resemble chlorides, bromides and iodides.

Fluorides differ from the other halides in the following respects—

(i) AgCl, AgBr and AgI are insoluble in water as well as in nitric acid but AgF is soluble in water.

(ii) CaF_2 and BaF_2 are insoluble in water whereas the calcium and barium salts of HCl, HBr and HI are soluble in water.

• HYDROGEN CHLORIDE (HCl) •

This acid was first obtained by **Priestly** in 1772 from sea salt and called it *muriatic acid.* In 1810 **Davy** proved that this acid was a compound of hydrogen and chlorine and termed it *hydrogen chloride.* Hydrochloric acid occurs in small quantities in the gastic juice of human and animals.

7.20. Preparation of hydrogen chloride.

1. Laboratory method :

[A] **Principle :** Hydrogen chloride is prepared by heating *common salt (sodium chloride) with conc. H_2SO_4.* The reaction takes place in two steps.

(i) At 150°C sodium chloride reacts with conc. H_2SO_4 to form *sodium bisulphate* and *hydrogen chloride.*

$$NaCl + H_2SO_4 = NaHSO_4 + HCl\uparrow$$

(ii) As above 500°C the produced sodium bisulphate reacts with the unreacted sodium chloride to form *sodium sulphate* and more *hydrogen chloride.*

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl\uparrow$$

In the laboratory the first stage of reaction is employed to prepare hydrogen chloride.

[B] **Procedure :** Sodium chloride is taken in a round bottomed flask fitted with a thistle funnel and a delivery tube. The lower end of the thistle funnel reaches up to the bottom of the flask. The flask is clamped to a stand and is placed on a wire gauze kept on a tripod stand. Conc. H_2SO_4 is then poured down the thistle funnel so that the end of the thistle funnel as well as the salt remain under the acid level. The flask is then heated gently when hydrogen chloride gas is evolved.

[C] **Purification :** The evolved hydrogen chloride coming out of the delivery tube is contaminated with moisture. It is passed through a washer bottle containing conc. H_2SO_4 where the moisture is absorbed. The dry gas then collected in a dry gas jar by the *upward displacement of air.*

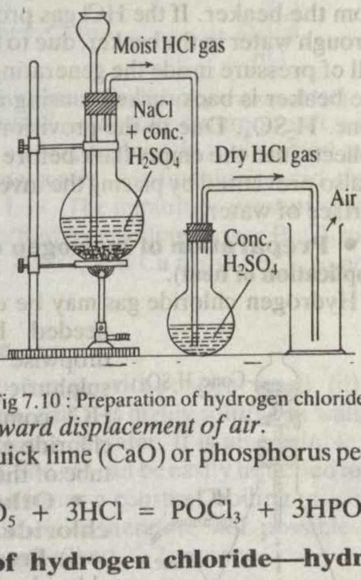


Fig 7.10 : Preparation of hydrogen chloride

Hydrogen chloride gas can not be dried by quick lime (CaO) or phosphorus pentoxide as both of them react with HCl.

$$CaO + 2HCl = CaCl_2 + H_2O, \qquad 2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$$

• Preparation of aqueous solution of hydrogen chloride—hydrochloric acid.

The aqueous solution of hydrogen chloride is called hydrochloric acid. It is prepared by dissolving hydrogen chloride in water.

At first hydrogen chloride gas is prepared in a round bottomed flask by the above mentioned process. The issuing gas is then led through an empty conical flask. The open end of the delivery tube which comes out of the conical flask is fitted with a glass funnel. The mouth of the funnel just dips under the surface of water in a beaker. The evolved hydrogen chloride gas is absorbed in the water of the beaker. When the process is continued for sometime, the solution becomes saturated. Thus a concentrated solution of hydrochloric acid is obtained.

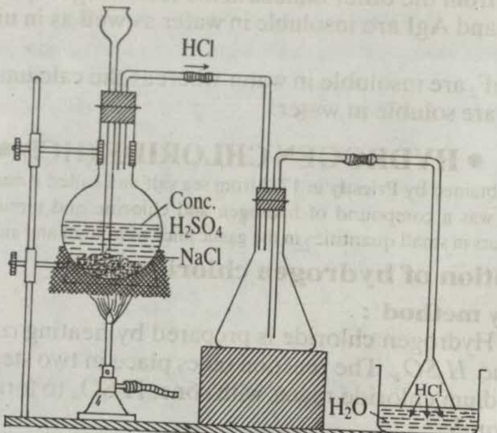


Fig. 7.11 : Preparation of hydrochloric acid

The purpose of placing the empty conical flask between the generating flask and beaker full of water, is to guard against any suction of water into the generating flask from the beaker. If the HCl gas produced in the generating flask is directly passed through water in the beaker, due to the great solubility of HCl gas in water, a sudden fall of pressure inside the generating flask may occur and as a result the water from the beaker is back sucked causing an explosion by coming in contact with hot and conc. H_2SO_4. Due to the provision of empty flask if the water is sucked back, it collects into the empty flask before entering the generating flask. The back suction is also prevented by placing the inverted funnel, the mouth of which just reaches the surface of water.

- **Preparation of hydrogen chloride at room temperature (without the application of heat).**

Hydrogen chloride gas may be easily obtained at room temperature whenever needed by adding concentrated hydrochloric acid dropwise from a dropping funnel to concentrated sulphuric acid taken in a filtering flask. As soon as conc. HCl comes in contact with conc. H_2SO_4, hydrogen, chloride gas begins to evolve which comes out of the side tube of the filtering flask.

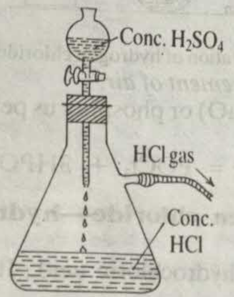


Fig 7.12 : Preparation of HCl at room temperature

- **Other methods of preparation of hydrogen chloride.**

(i) **From non-metallic chlorides :** Some non- metallic chlorides like *phosphorus trichloride, silicon tetrachloride* on being treated with water give hydrogen chloride.

$$PCl_3 + 3H_2O = 3HCl\uparrow + H_3PO_3$$
$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl\uparrow$$
$$PCl_5 + H_2O = 2HCl + POCl_3$$

(ii) **From metallic chlorides :** Hydrogen chloride is obtained by heating metallic chlorides with conc. H_2SO_4.

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl\uparrow$$
$$CuCl_2 + H_2SO_4 = CuSO_4 + 2HCl\uparrow$$

- **Manufacture of hydrochloric acid.**

1. **Synthetic method :** Now a days commercial HCl is manufactured by synthetic method which is based on the direct combination of chlorine and hydrogen.

$$H_2 + Cl_2 = 2HCl$$

The constituent elements i.e., hydrogen and chlorine are obtained as by-products during the manufacture of caustic soda by electrolytic process. Consequently the process is quite economic.

In this process chlorine is burnt in an atmosphere of hydrogen in a combustion chamber made of silica bricks. The hydrogen chloride formed is led through cooling pipes cooled by spray of water. The cooled gas is then led up an absorption tower packed with quartz, down which water flows in the form of spray. The solution of hydrochloric is collected from the bottom of the tower. The product is pure hydrochloric acid.

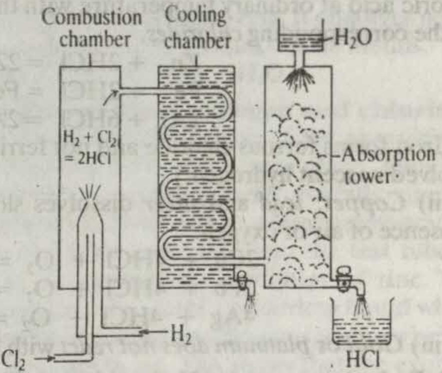


Fig 7.13 : Synthetic method of preparation of HCl

2. **By Leblanc process :** Hydrochloric acid is obtained as a by-product in the manufacture of sodium carbonate by Leblanc process. In India hydrochloric acid is manufactured by heating common salt with conc. H_2SO_4 in a cast iron vessel. The evolved hydrogen chloride is absorbed in a series of glazed earthenware vessels containing water. Hydrochloric acid thus obtained is 28% pure having specific gravity = 1·14. The impurities present in the acid are As_2O_3, $FeCl_3$ and H_2SO_4. The acid is purfied by distilling it over $BaCl_2$ and Cu turnings. $BaCl_2$ converts H_2SO_4 to insoluble $BaSO_4$ and Cu turns $FeCl_3$ to non volatile ferrous chloride.

7.21. Properties of hydrogen chloride.

[A] **Physical :** (i) Hydrogen chloride is a colourless gas with pungent smell. (ii) It is heavier than air and fumes strongly in moist air. (iii) It is highly soluble in water. About 450 volumes of HCl gas dissolve in 1 volume of water. It is also soluble in organic solvents like alcohol, acetic acid etc. (iv) The gas can be easily liquefied into colourless liquid which boils at 83°C (v) The gas forms a constant boiling mixture with water when it contains 22·2% of the acid. It is therefore not possible to concentrate an aqueous solution of HCl by boiling beyond 22·2 percent.

[B] **Chemical :**

1. **Combustibility :** It is neither combustible nor a supporter of combustion.

2. **Acidic nature :** Hydrogen chloride in gaseous state is not acidic, but the aqueous solution of the gas is highly acidic and one of the strongest acids. Hydrochloric acid is a monobasic acid and turns blue litmus red. It ionises completely in its

aqueous solution. In fact it is not the simple H^+ ion, but hydroxonium ion H_3O^+ is responsible for its acidic property.

$$HCl \rightleftharpoons H^+ + Cl^-, \qquad H^+ + H_2O = [H_3O]^+$$

(a) **Action on bases :** Hydrochloric acid reacts with *metallic oxides* and *hydroxides* forming the corresponding *chlorides* and *water*.

$$\begin{array}{ll} CaO + 2HCl = CaCl_2 + H_2O, & NaOH + HCl = NaCl + H_2O \\ Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O & MgO + 2HCl = MgCl_2 + H_2O \end{array}$$

(b) **Action of metallic carbonates and bicarbonates :** It reacts with metallic carbonates and bicarbonates with the evolution of CO_2.

$$\begin{array}{l} Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O \\ NaHCO_3 + HCl = NaCl + CO_2 + H_2O \end{array}$$

(c) **Action on metals :** (i) *The metals which are above hydrogen in the electrochemical* series (Mg, Zn, Al, Fe, Sn etc.) with the exception of Pb, react with hydrochloric acid at ordinary temperature with the evolution of *hydrogen* and formation of the corresponding *chlorides*.

$$\begin{array}{l} Zn + 2HCl = 2ZnCl_2 + H_2 \\ Fe + 2HCl = FeCl_2 + H_2 \\ 2Al + 6HCl = 2AlCl_3 + 3H_2 \end{array}$$

[Iron forms ferrous chloride and not ferric chloride due to the reducing action of evolved nascent hydrogen.]

(ii) *Copper, lead* and *silver* dissolves slowly on boiling with conc. HCl in the presence of air or oxygen.

$$\begin{array}{l} 2Cu + 4HCl + O_2 = 2CuCl_2 + 2H_2O \\ 2Pb + 4HCl + O_2 = 2PbCl_2 + 2H_2O \\ 4Ag + 4HCl + O_2 = 4AgCl + 2H_2O \end{array}$$

(iii) *Gold* or *platinum does not react* with hydrochloric acid.

3. **Reducing property :** Hydrochloric acid can reduce strong oxidising agents itself being oxidised to chlorine. Thus *manganese dioxide, lead dioxide* and *potassium dichromate* are reduced by conc. HCl on boiling.

$$\begin{array}{l} \overset{+4}{Mn}O_2 + 4H\overset{-1}{Cl} = \overset{+2}{Mn}Cl_2 + \overset{0}{Cl_2} + 2H_2O \\ \overset{+4}{Pb}O_2 + 4HCl = \overset{+2}{Pb}Cl_2 + \overset{0}{Cl_2} + 2H_2O \end{array}$$

$$\begin{array}{lll} & K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O & \\ 6HCl & + 3O & = 3Cl_2 + 3H_2O \\ K_2O & + 2HCl & = 2KCl + H_2O \\ Cr_2O_3 & + 6HCl & = 2CrCl_3 + 3H_2O \\ \hline K_2\overset{+6}{Cr_2}O_7 & + 14H\overset{-1}{Cl} & = 2KCl + 2\overset{+3}{Cr}Cl_3 + 3\overset{0}{Cl_2} + 7H_2O \end{array}$$

At ordinary temperature conc. HCl is oxidised by *potassium permanganate* to chlorine.

$$\begin{array}{lll} & 2KMnO_4 = K_2O + 2MnO + 5O & \\ 10HCl & + 5O & = 5Cl_2 + 5H_2O \\ K_2O & + 2HCl & = 2KCl + H_2O \\ 2MnO & + 4HCl & = 2MnCl_2 + 2H_2O \\ \hline 2K\overset{+7}{Mn}O_4 & + 16H\overset{-1}{Cl} & = 2KCl + 2\overset{+2}{Mn}Cl_2 + 5\overset{0}{Cl_2} + 8H_2O \end{array}$$

Conc. HCl is oxidised catalytically by aerial O_2 in presence of *cupric chloride*.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

4. **Stability :** HCl is quite stable but thermally dissociated to give H_2 and Cl_2 at about 1500°C.

5. **Action on ammonia :** It forms dense white fumes of ammonium chloride (solid) with ammonia. This reaction is *an example of the formation of a solid product by the action of two gases.*

$$HCl(g) + NH_3(g) = NH_4Cl(s)$$

6. **Precipitation reaction :** Hydrochloric acid on being added to the solution of a soluble salt of *silver or lead (II)* or *mercury (I)*, yields the corresponding *chloride as curdy white precipitate.*

$$AgNO_3 + HCl = AgCl\downarrow + HNO_3$$
$$Pb(NO_3)_2 + 2HCl = PbCl_2\downarrow + 2HNO_3$$
$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2\downarrow + 2HNO_3$$

7. **Action on conc. HNO_3 :** Three volumes of conc. HCl react with 1 volume of conc. HNO_3 to produce nitrosyl chloride with the evolution of nascent chlorine. This mixture of conc. HCl and conc. HNO_3 is known as *aqua regia.* It dissolves noble metals like gold, platinum. The evolved nascent chlorine attacks those metals.

$$3HCl + HNO_3 = NOCl + 2Cl\uparrow + 2H_2O$$

• To prove that hydrogen chloride contains hydrogen and chlorine.

(i) Some distilled water is taken in a test tube and 2 or 3 pieces of zinc granules are added to it. It is observed that even on heating no reaction takes place. Thus it is proved that inspite of the presence of hydrogen in water molecule, metallic zinc can not replace it from water i.e., water does not react with zinc at ordinary temperature to evolve hydrogen. Now on addition of a little conc. HCl into the test tube, a colourless and odourless gas is found to evolve with the dissolution of zinc. The evolved gas burns with a blue flame when ignited to form a colourless liquid which turns anhydrous white $CuSO_4$ blue. Thus it is proved that liquid is water which is formed due to the burning of the colourless gas in air. This shows that the evolved gas is hydrogen and this hydrogen has come from hydrochloric acid.

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow$$

(ii) A mixture of conc. HCl and MnO_2 is taken in a test tube, and the test tube is heated. A greenish yellow gas having the smell of bleaching powder is found to evolve. The evolved gas is passed through an aqueous solution of KBr when the colourless solution turns red due to the liberation of free bromine. When a filter paper soaked in starch iodide solution is held in the greenish yellow gas, the paper turns blue. Thus it is proved that the greenish yellow gas is chlorine and this chlorine has come from hydrogen chloride.

$$4HCl + MnO_2 = MnCl_2 + Cl_2 + 2H_2O$$
$$2KBr + Cl_2 = 2KCl + Br_2$$
$$Cl_2 + 2KI = 2KCl + I_2$$
$$I_2 + \text{Starch} \rightarrow \text{turns blue.}$$

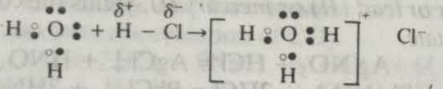
• Prove that conc. hydrochloric acid can act as a reducing agent.

Conc. hydrochloric acid is taken in a test tube and few cystals of potassium permanganate are added to it. As soon as the crytals of $KMnO_4$ come in contact with conc. HCl, a greenish yellow gas having the smell of bleaching powder begins to evolve. A filter paper soaked in KI and starch solution is held in the evolved gas when the paper turns blue. Thus it is proved that the greenish yellow gas is chlorine which is produced by the oxidation of HCl by $KMnO_4$. As HCl is oxidised, it has reduced $KMnO_4$ to colourless manganous salt.

$$2K\overset{+7}{Mn}O_4 + 16H\overset{-1}{Cl} = 2KCl + 2\overset{+2}{Mn}Cl_2 + 5\overset{0}{Cl_2} + 8H_2O$$

• Hydrogen chloride is a covalent compound but its aqueous solution can conduct electricity—explain why.

As the electronegativity of chlorine is greater than that of hydrogen, the electron pair forming the covalent bond between H and Cl atom is attracted towards that Cl atom. As a result the electron pair constituting the covalent bond between H and Cl atom is shifted towards Cl atom and thus Cl end of HCl becomes slightly negatively charged and the H end becomes slightly positively charged and thus HCl molecule becomes polar. $\overset{\delta^+}{H} + \overset{\delta^-}{Cl}$. Water molecule contains lone pair of electrons. When HCl is dissolved in water the proton H^+ from HCl molecule is detached and O atom of water molecule donates a pair of electrons to the proton. As a result hydroxonium ion is formed. Thus the aqueous solution of HCl contain H_3O^+ and Cl^- ions and so it can conduct electricity.



$$H:\underset{\underset{H}{\cdot\cdot}}{\overset{\cdot\cdot}{O}}: + \overset{\delta^+}{H} - \overset{\delta^-}{Cl} \rightarrow \left[H:\underset{\underset{H}{\cdot\cdot}}{\overset{\cdot\cdot}{O}}:H\right]^+ \quad Cl^-$$

7.22. Tests of hydrochloric acid and chlorides.

(i) When a glass rod moistened with strong NH_4OH is held in hydrogen chloride, a dense white fumes of NH_4Cl are produced.

$$HCl + NH_4OH = NH_4Cl + H_2O$$

(ii) Hydrochloric acid (conc.) on being treated with MnO_2 gives chlorine which turns starch iodide paper blue.

(iii) An aqueous solution of HCl or a chloride gives a curdy white precipitate of silver chloride with silver nitrate solution. The precipitate is insoluble in nitric acid but is readily soluble in excess of ammonium hydroxide solution forming a soluble complex salt.

$$\begin{aligned} AgNO_3 + HCl &= AgCl + HNO_3 \\ AgNO_3 + NaCl &= AgCl + NaNO_3 \\ AgCl + 2NH_4OH &= \underset{\substack{\text{Complex salt} \\ \text{soluble.}}}{[Ag(NH_3)_2]Cl} + H_2O \end{aligned}$$

(iv) *Chromyl chloride test :* On heating a chloride salt with solid potassium dichromate and conc. H_2SO_4, red vapours of chromyl chloride are produced.

$$\begin{aligned} K_2Cr_2O_7 + 2H_2SO_4 &= 2KHSO_4 + 2CrO_3 + H_2O \\ [KCl + H_2SO_4 &= KHSO_4 + HCl] \times 4 \\ [CrO_3 + 2HCl &= CrO_2Cl_2 + H_2O] \times 2 \\ \hline K_2Cr_2O_7 + 4KCl + 6H_2SO_4 &= 6KHSO_4 + \underset{\text{Chromyl chloride}}{2CrO_2Cl_2} + 3H_2O \end{aligned}$$

When the vapours of chromyl chloride are passed through NaOH solution, a yellow solution of sodium chromate is produced. which on treatment with lead acetate a yellow precipitate of lead chromate is obtained.

$$\begin{aligned} CrO_2Cl_2 + 2NaOH &= Na_2CrO_4 + 2HCl \\ (CH_3COO)_2Pb + Na_2CrO_4 &= 2CH_3COONa + \underset{\text{yellow ppt.}}{PbCrO_4 \downarrow} \end{aligned}$$

7.23. Uses of hydrochloric acid.

Hydrochloric acid is used—

(i) in the manufacture of various chloride salts and chlorine,
(ii) in pickling iron sheets before galvanising or tinning,
(iii) in the textile and dyeing industry,
(iv) in the preparation of *aqua regia* for dissolving metals like gold and platinum,
(v) as a reagent for the detection of acid and basic radicals in qualilative analysis,
(vi) for the extraction of glue from bones and animal tissues,
(vii) in medicine.

• Chlorides.

Salts of hydrochloric acid are known as chlorides.

Preparation :

1. **By direct combination of elements with chlorine.**

(a) Non-metals like sulphur, phosphorus and antimony combines directly with chlorine at ordinary temperature with the formation of the corresponding chlorides.

$$2S + Cl_2 = S_2Cl_2, \qquad 2P + 3Cl_2 = 2PCl_3, \qquad 2Sb + 3Cl_2 = 2SbCl_3$$

(b) Metal like Al, Fe, tin and zinc combine with Cl_2 when chlorine is passed over the heated metals with the formation of the corresponding chlorides.

$$2Al + 3Cl_2 = 2AlCl_3, \qquad 2Fe + 3Cl_2 = 2FeCl_3, \qquad Sn + 2Cl_2 = SnCl_4$$

2. **By the action of hydrochloric acid on metals metallic oxides and carbonates.**

$$Mg + 2HCl = MgCl_2 + H_2, \qquad CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$
$$2Al + 6HCl = 2AlCl_3 + 3H_2, \qquad NaOH + HCl = NaCl + H_2O$$

3. **By double decomposition :** When a soluble chloride is treated with the aqueous solution of the salts of silver, mercurous and lead, the corresponding chlorides are precipitated.

$$AgNO_3 + NaCl = AgCl \downarrow + NaNO_3$$
$$Hg_2(NO_3)_2 + 2KCl = Hg_2Cl_2 \downarrow 2KNO_3$$

Properties :

1. **Solubility :** Most of the chlorides with the exception of chlorides of Ag, Hg (*ous*), Pb and Cu (*ous*), are soluble in water. Lead chloride is soluble in boiling water.

2. **Action of heat :** Some hydrated chlorides like $AlCl_3$ $6H_2O$, $FeCl_3$ $6H_2O$ liberate hydrogen chloride when heated. Cupric chloride gives chlorine.

$$2FeCl_3, 6H_2O = Fe_2O_3 + 6HCl \uparrow + 3H_2O$$

3. **Hydrolysis :** Non metallic chlorides and metallic chlorides are hydrolysed in their aqueous solution. Chlorides of antimony and bismuth are partially hydrolysed to give oxychlorides.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl, \qquad BiCl_3 + H_2O = BiOCl + 2HCl$$

• HYDRO BROMIC ACID (HBr) •

(Hydrogen Bromide)

Formula : HBr	**Mol. wt. = 80·9**

7.24. Preparation of hydrogen bromide.

• HCl is prepared by heating a chloride salt (NaCl or KCl) with conc. H_2SO_4, but HBr cannot be prepared by heating a bromide salt with conc. H_2SO_4—explain why.

Conc. H_2SO_4 is an oxidising agent. On heating, conc. H_2SO_4 is thermally decomposed to give nascent oxygen and SO_2.

$$H_2SO_4 = H_2O + SO_2 + O$$

When NaCl is heated with conc. H_2SO_4 hydrogen chloride is produced but as the difference in the electronegativities of chlorine and oxygen is not high it is not possible for the oxygen evolved from H_2SO_4 to oxidise HCl to chlorine. But as the electronegativity of oxygen is much higher than that of bromine the HBr produced by the action of NaBr and conc. H_2SO_4 is easily oxidised by the nascent oxygen liberated by the thermal decomposition of conc. H_2SO_4 to free bromine. Consequently it not possible to prepare HBr by heating a bromide with conc. H_2SO_4.

$$NaBr + H_2SO_4 = NaHSO_4 + HBr$$
$$H_2SO_4 = H_2O + SO_2 + O$$
$$2HBr + O = H_2O + Br_2 \uparrow$$

1. Laboratory method :

[A] **Principle :** In the laboratory hydrogen bromide is prepared by the action of *bromine on red phosphorus in presence of water*. In the first step bromine reacts with red phosphorus to produce phosphorus tribromide and pentabromide. In the second step the produced PBr_3 and PBr_5 suffer hydrolysis with the formation of hydrogen bromide together with phosphorus acid and phosphoric acid respectively.

(i) $P_4 + 6Br_2 = 4PBr_3$, $\quad P_4 + 10Br_2 = 4PBr_5$

(ii) $PBr_3 + 3HOH = 3HBr + H_3PO_3$, $\quad PBr_5 + 4H_2O = 5HBr + H_3PO_4$

[B] **Procedure :** A mixture of red phosphorus and water is taken in a round bottomed flask. The mouth of the flask is fitted with a cork through which a dropping funnel and a delivery tube are inserted. The flask is clamped to stand and is kept on a wire gauze on a tripod stand. The delivery tube is connected successively with two U-tubes—the first one containing glass beads covered with moist red phosphorus and the second containing anhydrous calcium chloride. A bent delivery tube is fitted with the second U-tube, the end of which reaches almost the bottom of a upright dry gas jar. Now bromine is taken in the dropping funnel and it is added drop by drop into the mixture of red phosphorus and water. When vigorous reaction sets in with the evolution of hydrogen bromide gas.

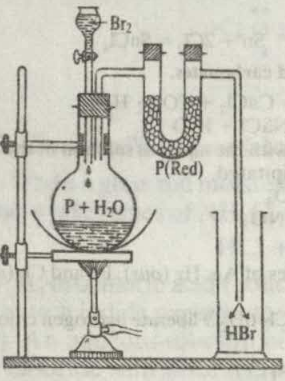


Fig 7.14 : Laboratory method of preparation of HBr

[C] **Purification :** The issuing hydrogen bromide gas contains bromine vapour and water. It is passed through the first U-tube where bromine vapour is eliminated. The water vapour is absorbed in the second U-tube by anhydrous $CaCl_2$.

The pure and dry hydrogen bromide is collected by the upward displacement of air.

- **Hydrogen bromide cannot be dried by conc. H_2SO_4 or CaO—explain why.**

Hydrogen bromide cannot be dried by conc. H_2SO_4. This is due to the fact that though conc. H_2SO_4 is a strong dehydrating agent—it is at the same time a strong oxidising agent. It oxidises the hydrogen bromide to bromine. Consequently it cannot be used for drying HBr.

$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$$

CaO is a basic oxide and so it is not possible to dry HBr by CaO as HBr reacts with CaO to form $CaBr_2$.

$$CaO + 2HBr = CaBr_2 + H_2O$$

2. **Preparation of aqueous solution of hydrogen bromide.**

The aqueous solution of hydrogen bromide is called hydrobromic acid. An aqueous solution of hydrogen bromide is prepared by the same process as described earlier in the preparation of hydrochloric acid.

3. **Preparation of hydrobromic acid from bromine.**

(a) Hydrogen sulphide gas is passed through bromine water when bromine is reduced by H_2S to give colourless hydrobromic acid and H_2S is oxidised by Br_2 to produce the precipitate of sulphur. The sulphur thus produced is separated by filtration and an aqueous solution of hydrobromic acid is obtained as filtrate.

$$H_2S + Br_2 = 2HBr + S\downarrow$$

(b) An aqueous solution of hydrobromic acid may also be prepared by passing sulphur dioxide gas through bromine water till it is decolourised. The resultant solution is treated with barium bromide when the produced H_2SO_4 is precipitated as insoluble $BaSO_4$. It is separated by filtration when a colourless solution of HBr is obtained as filtrate.

$$SO_2 + 2H_2O + Br_2 = H_2SO_4 + HBr$$
$$H_2SO_4 + BaBr_2 = BaSO_4\downarrow + 2HBr$$

(c) **Synthetic method** : Hydrogen and bromine do not combine together even in bright sunlight. When a mixture of hydrogen and bromine vapour is passed over a platinum spiral heated to redness by passing electric current, hydrogen bromide is produced.

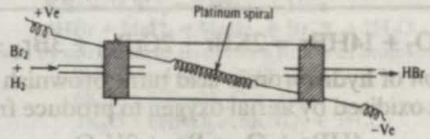


Fig 7.15 : Synthetic method of preparation of HBr

7.25. Properties of hydrogen bromide and hydrobromic acid.

[A] **Physical :** (i) Hydrogen bromide is a colourless gas having pungent odour. (ii) It is heavier than air. (iii) It is highly soluble in water and fumes in moist air. (iv) An aqueous solution containing 48% of HBr forms a constant boiling mixture.

[B] **Chemical :** (1) **Stability** : When hydrogen bromide is heated to 800°C, it decomposes into its constituent elements.

$$2HBr = H_2 + Br_2$$

(2) Its vapour is neither combustible nor a supporter of combustion.

(3) **Acidic property** : Hydrogen bromide does not exhibit acid property but its aqueous solution exhibits acid property. Hydrobromic acid is a strong monobasic acid. It turns blue litmus red.

(a) It reacts with *many metals* to form the corresponding *metal bromides* with the evolution of hydrogen.

$$Zn + 2HBr = ZnBr_2 + H_2, \qquad Mg + 2HBr = MgBr_2 + H_2$$

(b) Hydrobromic acid decomposes *carbonates* and *bicarbonates* to form the corresponding *bromides* with the evolution of carbon dioxide.

$$Na_2CO_3 + 2HBr = 2NaBr + CO_2 + H_2O$$
$$NaHCO_3 + HBr = NaBr + CO_2 + H_2O$$

(c) It reacts with bases to form *bromide salts*.

$$NaOH + HBr = NaBr + H_2O$$
$$CaO + 2HBr = CaBr_2 + H_2O$$

(4) **Action on ammonia** : It forms white fumes of *ammonium bromide* (solid) with ammonia.

$$HBr\,(g) + NH_3\,(g) = NH_4Br\,(s)$$

(5) **Reducing action** : As hydrogen bromide is more easily decomposed it acts as reducing agent. Thus manganese dioxide is reduced by HBr to form *manganous salt*, *potassium permanganate* is reduced to colourless *manganous salt*. *Chlorine* is reduced to *hydrochloric acid* and conc. H_2SO_4 to *sulphur dioxide*.

$$4H\overset{-1}{Br} + \overset{+4}{Mn}O_2 = \overset{+2}{Mn}Br_2 + \overset{0}{Br}_2 + 2H_2O$$
$$16HBr + 2KMnO_4 = 2KBr + 2MnBr_2 + 5Br_2 + 8H_2O$$
$$2HBr + Cl_2 = 2HCl + Br_2$$
$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$$

It reduces potassium dichromate to green coloured chromic chloride.

$$\begin{aligned}
K_2Cr_2O_7 &= K_2O + Cr_2O_3 + 3O \\
6HBr + 3O &= 3H_2O + 3Br_2 \\
K_2O + 2HBr &= 2KBr + H_2O \\
Cr_2O_3 + 6HBr &= CrBr_3 + 3H_2O \\
\hline
K_2\overset{+6}{Cr_2}O_7 + 14HBr &= 2KBr + 2\overset{+3}{Cr}Br_3 + 3Br_2 + 7H_2O
\end{aligned}$$

An *Aqueous solution* of hydrobromic acid turns brownish red when exposed to air and sunlight as it is oxidised by aerial oxygen to produce free bromine.

$$4HBr + O_2 = Br_2 + 2H_2O$$

(6) **Action with silver nitrate :** Aqueous solution of hydrobromic acid reacts with *silver nitrate solution* to give a *pale yellow precipitate* of *silver bromide* which is insoluble in nitric acid but sparingly soluble in excess of ammonium hydroxide.

$$HBr + AgNO_3 = AgBr \downarrow + HNO_3$$

7.26. Test of hydrobromic acid and bromides.

(i) Hydrobromic acid or bromides on being heated with conc. H_2SO_4 gives off reddish brown vapours of bromine.

$$2HBr + H_2SO_4 = Br_2 \uparrow + SO_2 + 2H_2O$$
$$2KBr + 2H_2SO_4 = Br_2 \uparrow + K_2SO_4 + 2H_2O + SO_2$$

(ii) Hydrobromic acid or an aqueous solution of any metallic bromide is treated with chlorine water and the mixture is shaken with *carbon disulphide* or *carbon tetrachloride*, the organic liquid layer turns reddish brown. This is due to the dissolution of liberated bromine by the action of chlorine on HBr or a metallic bromide.

$$2KBr + Cl_2 = 2KCl + Br_2 \uparrow$$
$$2HBr + Cl_2 = 2HCl + Br_2 \uparrow$$

(iii) Hydrobromic acid or an aqueous solution of a metallic bromide on being treated with silver nitrate solution a pale yellow precipitate of silver bromide is obtained which is insoluble in HNO_3 but dissolves in excess of ammonium hydroxide with difficulty.

7.27. Uses of hydrobromic acid.

It is used in the laboratory as a reagent. It is also used in the preparation of bromide salts.

- **Prove that the hydrobromic acid contains bromine.**

A little hydrobromic acid is taken in a test tube and chlorine water is added to it. Now to this mixture carbon-disulphide is added and the mixture is shaken well. On standing the mixture for sometime, the CS_2 layer is separated from the aqueous solution. It is found that the CS_2 layer has turned to reddish brown. This is due to the fact that Cl_2 of chlorine water oxidises hydrobromic acid to bromine which dissolves in CS_2 and turns it reddish brown.

$$2HBr + Cl_2 = 2HCl + Br_2$$

- **Bromides :** The salts of hydrobromic acid are known as bromides.

Preparation :

(1) ***By the action of bromine on metals*** **:** Heated metals like Na, K, Ca, Zn etc., combine directly with bromine to form the corresponding bromides.

$$2Na + Br_2 = 2NaBr, \qquad Zn + Br_2 = ZnBr_2$$

(2) ***By the action of hydrobromic acid on metallic oxides, carbonates and hydroxides.***

$$CaO + 2HBr = CaBr_2 + H_2O$$
$$K_2CO_3 + 2HBr = 2KBr + CO_2 + H_2O$$

(3) By the action of bromine on boiling solution or caustic soda or caustic potash.

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O$$

- **Properties of bromides :**

(i) With the exception of bromides of silver, mercury (*ous*) lead and copper (*ous*), the bromides are mostly soluble.

(ii) On being heated with conc. H_2SO_4 and MnO_2, the bromides give reddish brown vapours of bromine.

$$KBr + H_2SO_4 = KHSO_4 + HBr$$
$$4HBr + MnO_2 = MnBr_2 + Br_2 \uparrow + 2H_2O$$

(iii) Bromides are oxidised by nitric acid to give brown fumes of bromine.

$$\begin{array}{c} 2HNO_3 = H_2O + 2NO + 3O \\ 6KBr + 3O = 3K_2O + 3Br_2 \\ 3K_2O + 6HNO_3 = 6KNO_3 + 3H_2O \\ \hline 8HNO_3 + 6KBr = 6KNO_3 + 3Br_2 + 2NO + 4H_2O \end{array}$$

(iv) Chlorine liberates bromine from bromides.

$$2NaBr + Cl_2 = 2NaCl + Br_2$$

(vi) With silver nitrate solution the bromides give pale yellow precipitate of silver bromide, which is insoluble in HNO_3 but sparingly soluble in excess of NH_4OH.

$$AgNO_3 + KBr = AgBr \downarrow + KNO_3$$

• HYDROGEN IODIDE—HYDROIODIC ACID •

An aqueous solution of hydrogen iodide is known as hydroiodic acid.

7.28. Preparation of hydrogen iodide.

1. **Laboratory method :**

[A] **Principle :** Hydrogen iodide is prepared in the laboratory by the action of water on a mixture of *red phosphorus* and *iodine at ordinary temperature*. The reaction takes place in two steps. (i) At first moist red phosphorus reacts with iodine to produce *phosphorus* tri-iodide. (ii) The produced phosphorus tri-iodide is then *suffers hydrolysis* with water to form *phosphorus acid and hydrogen iodide*.

$$\begin{array}{l} 2P + 3I_2 = 2PI_3 \\ [PI_3 + 3H{\cdot}OH = 3HI + H_3PO_3] \times 2 \\ \hline 2P + 3I_2 + 6H_2O = 6HI + 2H_3PO_3 \end{array}$$

[B] **Procedure :** (i) An intimate mixture of red phosphorus and iodine is taken in flask fitted with a dropping funnel and an outlet tube. (ii) The outlet tube is connected to two U-tubes in succession. The first U-tube contains glass beads coated with moist red phosphorus and the second U-tube is packed with phosphorus pentoxide. (iii) The second U-tube is connected with a delivery tube the end of which reaches almost the bottom of a dry gas jar. (iv) Water is allowed to fall drop by drop from the dropping funnel on the mixture when hydrogen iodide is evolved.

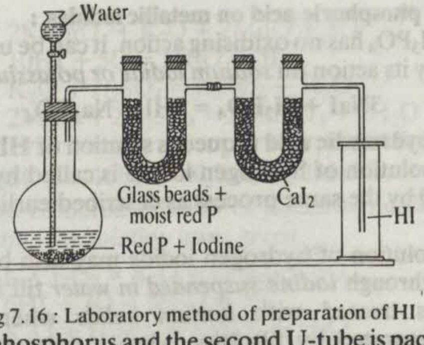


Fig 7.16 : Laboratory method of preparation of HI

[C] **Purification :** Hydrogen iodide thus produced is contaminated with iodine vapour and moisture. The evolved hydrogen iodide is passed through the first U-tube where iodine vapours are absorbed by the red phosphorus. It is next passed through the second U-tube where moistures are absorbed by P_2O_5. The HI gas being heavier than air, is collected in the gas jar by the upward displacement of air.

[**N.B.** (i) Hydrogen iodide can also be dried by anhydrous *calcium chloride*. But it can not be dried *CaO or conc. H_2SO_4*. This is due to the fact that as CaO is a basic oxide and HI being an acid, it reacts with CaO with the formation of CaI_2 and water. Conc. H_2SO_4 cannot be used for drying HI because due to the oxidising action of conc. H_2SO_4, it oxides HI to form free iodine.

$$CaO + 2HI = CaI_2 + H_2O$$
$$2HI + H_2SO_4 = I_2 + SO_2 + 2H_2O$$

- **Hydrogen iodide cannot be prepared by the action of conc. H_2SO_4 on metallic iodides (e.g., KI, NaI)—explain why.**

This is because of the fact that the hydrogen iodide produced by the action of iodides on hot and conc. H_2SO_4 is oxidised by the oxidising action of con. H_2SO_4 to free iodine. SO_2 is also produced due to the reduction of H_2SO_4 by HI.

$$NaI + H_2SO_4 = NaHSO_4 + HI$$
$$2HI + H_2SO_4 = I_2 + SO_2 + 2H_2O$$

(ii) *As hydrogen iodide is highly soluble in water, it cannot be collected by the displacement of water.* As HI attacks mercury it cannot be collected on mercury.

2. An aqueous solution of hydrogen iodide is prepared when hydrogen sulphide is passed slowly through iodine suspended in water till the colour of iodine disappears. Hydrogen sulphide reacts with iodine and reduces it to colourless hydroiodic acid.

$$H_2S + I_2 = 2HI + S$$

3. **Synthetic method :**

Hydrogen iodide is prepared by the direct combination of hydrogen and iodine. When a mixture of hydrogen and iodine-vapour is passed through a tube containing heated *platinised asbestos*, hydrogen and iodine combine together to form hydrogen iodide.

$$H_2 + I_2 \rightleftharpoons 2HI$$

This is a reversible reaction. As hydrogen iodide is less stable, it easily dissociates into its elements under the influence of heat, this process is seldom used in the preparation of HI.

4. **By the action of phosphoric acid on metallic iodides :**

As hot and conc. H_3PO_4 has no oxidising action, it can be used for the preparation of hydrogen iodide by its action on *sodium iodide or potassium iodide.*

$$3NaI + H_3PO_4 = 3HI + Na_3PO_4$$

5. **Preparation of hydroiodic acid** (aqueous solution of HI).

(a) The aqueous solution of hydrogen iodide is called hydroiodic acid. Hydroiodic acid is prepared by the same process as described earlier in the preparaton of hydrochloric acid.

(b) An aqueous solution of hydrogen iodide may also be prepared by passing *sulphur dioxide gas* through *iodine suspended in water* till it is decolourised. The resultant solution is treated with *barium iodide* when insoluble $BaSO_4$ is precipitated. It is separated by filtration when a colourless solutions of HI is obtained as filtrate.

$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI$$
$$H_2SO_4 + BaI_2 = BaSO_4 + 2HI$$

7.29. Properties of hydrogen iodide.

[A]. **Physical :**

(i) Hydrogen iodide is a colourless gas having pungent smell. It fumes in moist air. (ii) It is highly soluble in water and is heavier than air. (iii) It can be liquefied to a colourless liquid b.p. of which is −35·4°C. (iv) It forms a constant boiling mixture which boils at 127°C when the solution contains 57% of hydrogen iodide.

[B] **Chemical :**

1. **Stability :** It is the *least stable of all halogen acids.* It is easily decomposed to give hydrogen and violet vapours of iodine on heating. It also decomposes when it is exposed to sunlight.

$$2HI \rightleftharpoons H_2 + I_2$$

2. **Acidic property :** Hydroiodic acid is a strong monobasic acid and turns blue litmus red. It ionises completely in its aqueous solution.

$$HI \rightleftharpoons H^+ + I^-$$

(a) *Action on bases :* It reacts with *metallic oxides* and *hydroxides* forming the corresponding *iodides.*

$$CaO + 2HI = CaI_2 + H_2O, \qquad NaOH + HI = NaI + H_2O$$

(b) It reacts with *carbonates* with the evolution of *carbon dioxide.*

$$Na_2CO_3 + 2HI = 2NaI + CO_2 + H_2O$$

(c) It reacts with *many metals* with the evolution of hydrogen and producing *metallic iodides.*

$$Zn + 2HI = ZnI_2 + H_2, \qquad Mg + 2HI = MgI_2 + H_2$$

3. **Action on oxygen :** Hydroiodic acid is oxidised by the aerial oxygen in presence of sunlight to form water and iodine.

$$4HI + O_2\,(\text{air}) = 2H_2O + I_2$$

[This is why a freshly prepared colourless solution of hydroiodic acid when kept exposed in air, turns brown. The brown colour is due to dissolution of free iodine in hydroiodic acid.]

4. **Reducing property :** *Hydrogen iodide is a strong reducing agent.* In addition to the strong oxidising agents like $KMnO_4$, $K_2Cr_2O_7$, HNO_3, H_2O_2 etc., it is also oxidised by milder oxidising agents like $FeCl_3$, $CuSO_4$, HNO_2 etc. While reducing, hydroiodic acid itself is oxidised to give free iodine in each case.

(i) *Acidified solution of potassium permanganate* is reduced to give colourless *manganous salt.*

$$
\begin{aligned}
&2KMnO_4 + K_2O + 2MnO + 5O\\
&10HI + 5O = 5H_2O + 5I_2\\
&K_2O + H_2SO_4 = K_2SO_4 + H_2O\\
&2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O
\end{aligned}
$$

$$2K\overset{+7}{Mn}O_4 + 3H_2SO_4 + 10H\overset{-1}{I} = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 5\overset{0}{I_2} + 8H_2O$$

(ii) Acidified orange coloured solution of *potassium dichromate* is reduced to give *chromic salt* and thus the *solution turns green.*

$$
\begin{aligned}
&K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O\\
&6HI + 3O = 3H_2O + 3I_2\\
&K_2O + H_2SO_4 = K_2SO_4 + H_2O\\
&Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O
\end{aligned}
$$

$$K_2\overset{+6}{Cr_2}O_7 + 6H\overset{-1}{I} + 4H_2SO_4 = K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + 3\overset{0}{I_2} + 7H_2O$$

(iii) *Conc. HNO_3* is reduced to *nitrogen dioxide.*

$$2HNO_3 = H_2O + 2NO_2 + O$$
$$2HI + O = H_2O + I_2$$
$$\overline{2H\overset{+5}{N}O_3 + 2HI = I_2 + 2\overset{+4}{N}O_2 + 2H_2O}$$

(iv) *Hydrogen peroxide* is reduced to *H_2O.*

$$H_2O_2 + 2HI = 2H_2O + I_2$$

(v) Yellow solution of *ferric salts* are reduced to give a colourless solution of *ferrous salts.*

$$2FeCl_3 + 2HI = 2FeCl_2 + 2HCl + I_2$$
$$Fe_2(SO_4)_3 + 2HI = 2FeSO_4 + H_2SO_4 + I_2$$

(vi) *Copper sulphate* solution is reduced *cuprous iodide.*

$$2CuSO_4 + 4HI = 2CuI_2 + 2H_2SO_4$$
$$2CuI_2 = Cu_2I_2 + I_2$$
$$\overline{2CuSO_4 + 4HI = Cu_2I_2 + 2H_2SO_4 + I_2}$$

[HCl or HBr cannot reduce ferric salts to ferrous salt and $CuSO_4$ to Cu_2I_2. This proves that HI is a stronger reducing agent than HCl or HBr.]

(vii) *Nitrous acid is* reduced to *nitric oxide* and HI is oxidised to give free I_2.

$$2HNO_2 + 2HI = 2NO + I_2 + 2H_2O$$

(viii) *Stannic chloride* is reduced to *stannous chloride.*

$$SnCl_4 + 2HI = SnCl_2 + 2HCl + I_2$$

(ix) Conc. H_2SO_4 is reduced to *sulphur dioxide, sulphur* or to *H_2S* depending upon the amount of HI used.

$$H_2SO_4 + 2HI = I_2 + SO_2 + 2H_2O$$
$$H_2SO_4 + 6HI = 3I_2 + S + 4H_2O$$
$$H_2SO_4 + 8HI = 4I_2 + H_2S + 4H_2O$$

5. **Action on silver nitrate solution :** With *silver nitrate solution,* hydroiodic acid gives a *yellow precipitate of silver iodide.* This precipitate is insoluble in HNO_3 and NH_4OH.

[HCl on being treated with $AgNO_3$ solution gives a curdy white precipitate of AgCl which is insoluble in HNO_3 but soluble in excess of NH_4OH.

HBr forms a light yellow precipitate of AgBr. AgBr is insoluble in HNO_3 and sparingly soluble in excess of NH_4OH.]

6. **Action on lead acetate solution :** *Lead acetate* solution gives a *yellow precipitate of lead iodide* which is soluble in boiling water.

$$Pb(CH_3COO)_2 + HI = PbI \downarrow + 2CH_3COOH$$

7.30. Tests for hydrogen iodide and iodides.

(i) Hydroiodic acid and iodides give violet vapours of iodine on being heated with conc. H_2SO_4. A paper soaked in starch solution turns blue when comes in contact with this vapours.

$$H_2SO_4 = H_2O + SO_2 + O$$
$$2KI + O = K_2O + I_2$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O$$
$$\overline{2KI + 2H_2SO_4 = K_2SO_4 + SO_2 + I_2 \uparrow + 2H_2O}$$
$$2HI + H_2SO_4 = I_2 \uparrow + SO_2 + 2H_2O$$

(ii) An aqueous solution of HI and iodides on being treated with silver nitrate solution, gives a *yellow precipitate of silver iodide* which is insoluble in HNO_3 and NH_4OH.

$$NaI + AgNO_3 = NaNO_3 + AgI \downarrow$$

(iii) An aqueous solution of HI or iodides is treated with chlorine water and the mixture is shaken with CS_2 in a test tube. The layer of CS_2 turns violet on standing.

7.31. Uses of hydrogen iodide.

It is used as a reagent in the laboratory and as a reducing agent in organic chemistry. Potassium iodide is used as medicine and silver iodide is used in photography.

- **Iodides :**

Preparation : (i) The metallic iodides are prepared by the direct union of some metals with iodine.

$$Hg + I_2 = HgI_2$$

(ii) Iodides are also prepared by the action of HI on *metals, oxides, hydroxides* and *carbonates*.

$$2HI + Zn = ZnI_2 + H_2, \qquad NaOH + HI = NaI + H_2O$$
$$CaO + 2HI = CaI_2 + H_2O, \qquad Na_2CO_3 + 2HI = 2NaI + CO_2 + H_2O$$

(iii) By the action of iodine on strong alkali solution.

$$3I_2 + 6NaOH = 5NaI + NaIO_3 + 3H_2O$$

(iv) By the reduction of iodates.

$$KIO_3 + 3C = KI + 3CO$$

Properties : (i) Excepting the iodides of Ag, Hg (*ous*) Bi, and Pb all other iodides are soluble in water.

(ii) Iodides are less volatile than the corresponding chlorides and bromides.

(iii) The iodides have reducing properties.

(iv) The iodides on heating, are thermally decomposed to give free iodine.

(v) With soluble lead acetate solution a yellow precipitate of PbI is obtained.

$$2KI + Pb(CH_3COO)_2 = PbI_2 + 2CH_3COOK$$

(vi) An aqueous solution of an iodide on being treated with mercuric chloride, a scarlet precipitate of mercuric iodide is obtained.

$$HgCl_2 + 2KI = 2KCl + HgI_2 \downarrow$$

Uses : Iodides are used in medicine, photography and as a laboratory reagent.

- **Prove that hydrogen iodide contains iodine.**

An aqueous solution of hydrogen iodide is taken in a test tube and is treated with chlorine water. Some CS_2 is added to it and the mixture is shaken well. The layer of CS_2 turns violet on standing. Chlorine water liberates iodine from HI which dissolves in CS_2 yielding a violet solution. This violet solution turns starch solution blue which goes to prove the presence of iodine. This iodine has come from hydrogen chloride..

$$2HI + Cl_2 = 2HCl + I_2$$
$$I_2 + \text{Starch} \rightarrow \text{turns blue.}$$

- **Prove that HI is a stronger reducing agent than HCl or HBr.**

It is observed that conc. HCl cannot reduce conc. H_2SO_4 to SO_2. When HBr is reacted with conc. H_2SO_4, the later is reduced to SO_2 by HBr. In this reduction the oxidation number of S-atom in H_2SO_4 decreases from +6 to +4.

$$H_2\overset{+6}{S}O_4 + 2HBr = 2H_2O + Br_2 + \overset{+4}{S}O_2$$

HI reduces conc. H_2SO_4 to SO_2, sulphur, or to hydrogen sulphide, depending upon the amount of HI used.

$$H_2SO_4 + 2HI = I_2 + SO_2 + 2H_2O$$
$$H_2\overset{+6}{S}O_4 + 6HI = 3I_2 + \overset{0}{S} + 4H_2O$$
$$H_2\overset{+6}{S}O_4 + 8HI = 4I_2 + H_2\overset{-2}{S} + 4H_2O$$

Thus it is observed that the oxidation number of S-atom in H_2SO_4 decreases from +6 to +4 or 0 or −2. This proves that in case of HI the extent of reduction of H_2SO_4 is much greater than that of HBr. Consequently HI is stronger reducing agent than HCl or HBr.

• Aqueous solutions of HF, HCl, HBr and HI are kept in a different polythene bottles. How would you identify these acids ?

The 4 acids can be identified by the following tests. The observations and inferences for each test are given below.

Experiment	**OBSERVATIONS**			
	HF	**HCl**	**HBr**	**HI**
(i) The sample is heated with MnO_2.	Fluorine gas does not evolve.	A greenish yellow gas having the smell of bleaching evolves which turns starch iodide paper blue—thus the evolved gas is Cl_2.	A reddish brown gas evolves which turns starch paper yellow—thus the evolved gas is bromine.	Violet vapours are evolved which turn starch blue.
(ii) To the solution of the sample $AgNO_3$ solution is added.	No precipitate is obtained.	A curdy white precipitate is obtained which is insoluble in HNO_3 but soluble in excess of NH_4OH.	A pale yellow precipitate is obtained which is insoluble in HNO_3 and sparingly soluble in excess of NH_4OH.	A yellow precipitate is obtained which is insoluble in HNO_3 and in NH_4OH.
(iii) To the solution of the sample $BaCl_2$ solution is added.	A white precipitate is obtained which is insoluble in HNO_3.	No precipitate is formed.	No precipitate is formed.	No precipitate is formed.
(iv) To an aqueous solution of the sample, chlorine water is added and the mixture is shaken with CS_2 in a test tube.	No change is observed in the CS_2 layer.	No change is observed in the CS_2 layer.	The layer of CS_2 turns reddish brown.	The layer of CS_2 turns violet.

• Comparison between HF, HCl, HBr and HI.

The halogen acids exhibit well marked gradation and similarities in their physical and chemical properties—excepting hydrogen fluoride which differs from the other halogen hydrides in many respects.

1. All the hydracids of halogen have identical formula and can be expressed by the general formula HX (X = F, Cl, Br, I). All of them are colourless.

2. Hydrogen fluoride is a colourless liquid below 19·5° while the rest of the halogen acids are gases which fumes in moist air.

3. **Stability :** The thermal stability of these hydracids decreases from HF to HI. Hydrogen fluoride is most stable. HCl is thermally decomposed at above 1500°C, HBr decomposes at 800°C into its constituent elements and HI is least stable. It is easily decomposed to H_2 and I_2 on heating or when it is exposed to sunlight.

4. The increasing order of boiling points and melting points of halogen hydracids are given below—

$$\text{m.p.}\quad HCl < HBr < HF < HI$$
$$\text{b.p.}\quad HCl < HBr < HI < HF$$

The solubility of the halogen hydracids increases from HCl to HI.

5. In gaseous state all the hydracids are covalent compounds as indicated by their low melting and boiling points and poor electrical conductivity in pure state. The molecules of these hydracids are polar. The increasing order of polarity is shown below— $H—I < H—Br < H—Cl < H—F$

6. **Hydrogen bond :** Due to the high electronegativity of fluorine, HF is capable of forming hydrogen bonding between their molecules and consequently hydrogen

fluoride is highly associated compound. HCl, HBr and HI cannot form hydrogen bonding between their molecules and as a result they are non-associated compounds.

7. All the halogen hydracids ionise in aqueous solution and give $(H_3O)^+$ ion.

$$HX \rightleftharpoons H^+ + X^- \qquad H^+ + X^- + H_2O \rightleftharpoons (H_3O)^+ + X^-$$

All the halogen hydracids are monobasic. Though HF is monobasic acid it forms $(HF_2)^-$ ion in its aqueous solution which is produced as a result of hydrogen bonding between F^- and HF molecule.

$$HF \rightleftharpoons H^+ + F^-$$
$$F^- + HF \rightleftharpoons (HF_2)^-$$

Thus inspite of being a monobasic acid, HF can form acid salts like KHF_2 *or* $NaHF_2$. *Other halogen hydracids can not form such acid salt.* In liquid state HF molecules are associated by hydrogen bonding and so HF in its aqueous solution ionises to a small extent so it behaves as a weak acid, whereas HCl, HBr and HI in their aqueous solution ionise completely and so they behave as strong acids. The relative strength of the halogen acids increases in the order given below—

$$HF < HCl < HBr < HI$$

8. As the electronegativity of fluorine is maximum, HF is not oxidised even by strongest oxidising agent. HCl can be oxidised by strong oxidising agents while HBr and HI are easily oxidised to give their corresponding halogens. Hydroiodic acid possesses reducing property.

9. **Solubility of some metallic halides :** Silver fluoride is soluble in water while silver chloride, silver bromide and silver iodide are insoluble in water as well as in HNO_3. Barium fluoride is insoluble in water whereas barium salts of other halogen are soluble in water.

10. HCl, HBr and HI can not form complex acids with boron and silicon, but HF forms complex acids with boron such as fluoboric acid HBF_4 and with silicon such as hydrofluo silicic acid H_2SiF_6.

11. HF reacts with silica, glass and silicates. HCl, HBr or HI have no action on these substances.

12. **Reducing property :** The reducing property of halogen acids increases from HF to HI. In HF molecule the F^- ion is very small and consequently the electron which is to be removed for its oxidation is so nearest to its nucleus, that it is very difficult to be removed. Thus it is very difficult for HF to be oxidised. As a result HF is a poor reducing agent. On the other hand due to the large size of I^- ion in HI the electrons are less tightly held and hence can be easily lost i.e., HI can be easily oxidised. Consequently HI is the strongest reducing agent among HX.

- **Comparative study of the properties of hydrogen halides :**

Property	HF	HCl	HBr	HI
(1) Physical state at N.T.P.	Liquid.	Gas.	Gas.	Gas.
(2) Colour of the gas or vapour	Colourless.	Colourless.	Colourless.	Colourless.
(3) Boiling point	19·4°C	−85°C	−66·7°	−35·4°
(4) Solubility at 0°C	miscible	42%	68%	90%
(5) Thermal stability	stable.	dissociates at 1500°C	dissociates at 800°C	dissociates at 180°C
(6) Acid property	Weak acid due to hydrogen bonding between its molecule.	Aqueous solution is strong acid.	Aqueous solution is stronger acid.	Aqueous solution is strongest acid.

Property	HF	HCl	HBr	HI
(7) Reducing property	Has no reducing property.	Acts as a reducing agent oxidised to Cl_2	Stronger reducing agent than HCl oxidised to Br_2	Strongest reducing agent of all the halogen acids.
(8) Solubility of silver salt in water	AgF is soluble	AgCl is insoluble.	AgBr is insoluble.	AgI is insoluble.

• Distinction among fluoride, chloride, bromide and iodide.

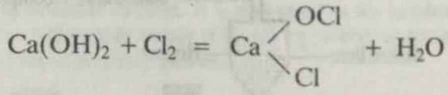
Experiment	OBSERVATIONS			
	Fluoride	**Chloride**	**Bromide**	**Iodide**
1. The solid is heated with conc. H_2SO_4 in a test tube	HF is given off which etches glass. The evolving gas turns a drop of water opalescent.	Colourless HCl is given off which forms dense white fumes with NH_3.	Reddish brown vapours of Br_2 are given off.	Violet vapours of iodine are given off.
2. The solid sample is heated with MnO_2 and H_2SO_4	F_2 is not liberated.	A greenish yellow gas evolves having the smell of bleaching powder, which turns starch iodide paper blue.	Reddish brown vapours of Br_2 are given off which turns starch iodide paper blue.	Violet vapours of iodine are given off which turns starch blue.
3. Aqueous solution of the sample is treated with $AgNO_3$ solution	No precipitate is formed.	A curdy white ppt. is obtained which is insoluble in HNO_3 but soluble in excess of NH_4OH.	A pale yellow ppt. is obtained which is insoluble in HNO_3 but sparingly soluble in excess of NH_4OH	A yellow ppt. is obtained which is insoluble in HNO_3 and in NH_4OH.
4. Aqueous solution of the sample is treated with $BaCl_2$ solution	A white ppt. is obtained.	No ppt.	No ppt.	No ppt.
5. Aqueous solution of the sample is shaken with Cl_2, water and CS_2	No colouration of CS_2 layer.	No colouration of CS_2 layer.	CS_2 layer turns reddish brown.	CS_2 layer turns violet.
Confirmatory test	Fluoride is heated with sand and conc. H_2SO_4. A drop of water on being exposed to the evolving gas turns opalescent	Chloride is heated with solid $K_2Cr_2O_7$ and conc. H_2SO_4—red fumes of chromyl chloride evolve	To the aqueous solution of a bromide, Cl_2, water and starch are added—the starch solution turns yellow	To the aqueous solution of iodide, Cl_2, water and starch are added—the starch turns blue

7.32. Some important oxycompounds of chlorine.

1. Bleaching powder or calcium chloro hypochlorite :

Manufacture of bleaching powder.

Bleaching powder is manufactured by the action of *chlorine on dry slaked lime.*



$$\mathrm{Ca(OH)_2 + Cl_2 = Ca}\begin{matrix}\diagup\mathrm{OCl}\\ \diagdown\mathrm{Cl}\end{matrix} + \mathrm{H_2O}$$

The temperature of this reaction should be kept below 40°C.

(i) **Hesenclever's plant :** The manufacture of Cl_2 is carried out in Hesenclever's plant. It consists of a number of horizontal cylinders made of cast iron. In each cylinder there is a rotating shaft fitted with blades. Slaked lime is fed into a hopper at the top. As the shaft rotates, the blades attached to it push the slaked lime from one end of the cylinder to the next cylinder. A current of dry chlorine is introduced through an inlet tube at the bottom which flows through the cylinders in the opposite direction of the flow of slaked lime. This counter current ensures the complete conversion of slaked lime into bleaching powder. Bleaching powder thus prepared comes out of the plant through an outlet tube in the lower most cylinder. The waste gases escape through an outlet tube in the topmost cylinder.

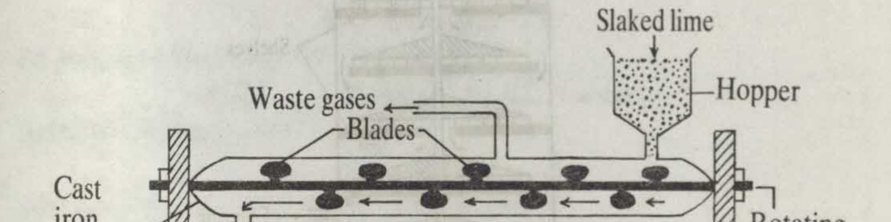


Fig 7.17 : Manufacture of bleaching powder by Hesenclever's process

(ii) **Bechmann's plant :** Bechmann's plant consists of a vertical cast iron tower fitted with eight shelves each containing rotating rakes. There is a hopper at the top of the tower and slaked lime is fed into the hopper. A stream of chlorine is introduced at the seventh shelf. The rotating racks push the slaked lime from one shelf to the other. Thus the added slaked lime moves downwards and meets the current of Cl_2 which is flowing up. Thus Cl_2 is completely absorbed by the slaked lime with the

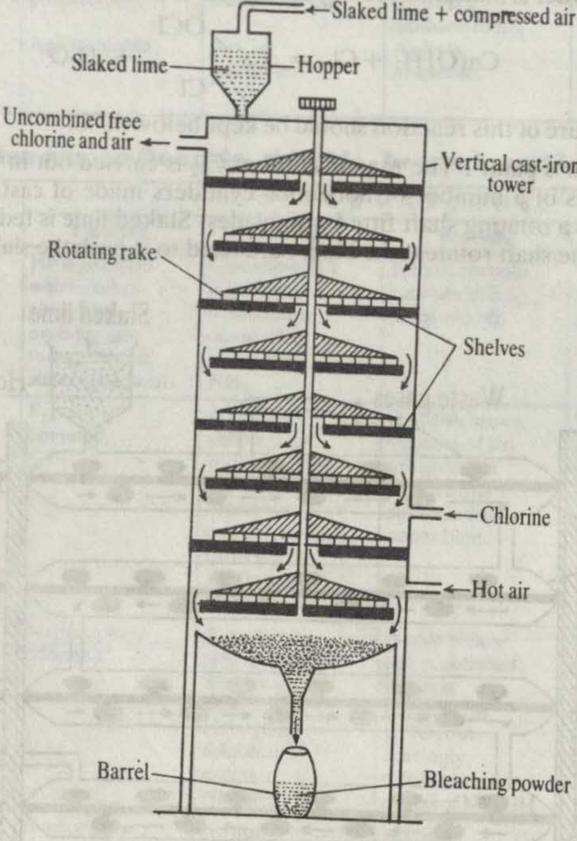


Fig 7.18 : Manufacture of bleaching powder by Bechmann's process

formation of bleaching powder. Bleaching powder thus produced is collected from the base. A current of hot air is blown into the eighth shelf to remove the unabsorbed chlorine which passes out of the exit tube at the top of the tower.

Properties : (i) It is white amorphous powder having a strong smell of chlorine. (ii) It is soluble in water, but as some unconverted slaked lime is always present in it, a clear solution is never obtained. Its aqueous solution confirms the presence of Ca^{++}, Cl^- and OCl^- ions. $Ca(OCl)Cl \rightleftharpoons Ca^{++} + Cl^- + OCl^-$. (iii) *Decomposition*—On standing long it undergoes slow decomposition with the formation of calcium chlorate and chloride.

$$6Ca(OCl)Cl = Ca(ClO_3)_2 + 5CaCl_2$$

(iv) In presence of cobalt chloride $CoCl_2$ (catalyst), it liberates oxygen.

$$2Ca(OCl)Cl = 2CaCl_2 + O_2$$

(v) With excess of dilute acids it evolves Cl_2.

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2$$
$$Ca(OCl)Cl + H_2SO_4 = CaSO_4 + H_2O + Cl_2$$

Even the carbonic acid present in moist air evolves Cl_2 from bleaching powder. This why it has a smell of chlorine.

$$Ca(OCl)Cl + H_2CO_3 = CaCO_3 + H_2O + Cl_2$$

● **Available chlorine :** The amount of chlorine which is liberated by the action of dilute acids on bleaching powder is known as available chlorine. It is expressed as the number of parts by weight of chlorine which is liberated from 100 parts by weight of bleaching powder on treatment with dilute acids. A good sample contains 35—37% of available chlorine.

● **Oxidising and bleaching action.**

On addition of dilute acid in small quantity, HOCl is produced which is decomposed to give nascent oxygen. This nascent oxygen is responsible for the oxidising and bleaching action of bleaching powder.

$$\begin{aligned} 2Ca(OCl)Cl + H_2SO_4 &= CaSO_4 + CaCl_2 + 2HOCl \\ HOCl &= HCl + O\uparrow \end{aligned}$$

(a) It oxidises KI to free iodine in presence of acetic acid.

$$Ca(OCl)Cl + 2CH_3COOH = Ca(CH_3COO)_2 + H_2O + Cl_2$$

$$2K\overset{-1}{I} + Cl_2 = 2KCl + \overset{0}{I_2}$$

(b) It oxidises sodium arsenite to sodium arsenate.

$$Na_3\overset{+3}{As}O_3 + Ca(OCl)Cl = Na_3\overset{+5}{As}O_4 + CaCl_2$$

(c) H_2S is oxidised to sulphur.

$$Ca(OCl)Cl + H_2\overset{-2}{S} = CaCl_2 + H_2O + \overset{0}{S}\downarrow$$

(d) Acidified ferrous sulphate is oxidised to ferric sulphate.

$$Ca(OCl)Cl + 2\overset{+2}{Fe}SO_4 + H_2SO_4 = \overset{+3}{Fe}_2(SO_4)_3 + CaCl_2 + H_2O$$

● **Bleaching action :** In presence of dilute acids it produces HOCl from which nascent oxygen is liberated. This nascent O bleaches the coloured substance by oxidation.

$$2Ca(OCl)Cl + H_2SO_4 = CaCl_2 + CaSO_4 + 2HOCl$$

$$HOCl = HCl + O$$

$$\text{Coloured substance} \xrightarrow{[O]} \text{bleached substance}$$

Uses : It is used (i) for bleaching cotton, linen, and wood pulp ; (ii) as disinfectant and germicide for drains and for sterilising drinking water ; (iii) in the manufacture of chloroform ; (iv) as oxidising agent in industry.

2. Sodium hypochlorite (NaOCl).

The sodium salt of hypochlorous acid is known as sodium hypochlorite.

(i) It is prepared by passing chlorine in cold and dilute solution of caustic soda.

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O$$

(ii) It is manufactured by electrolysing cold solution of sodium chloride (Brine solution). The aqueous solution of NaCl dissociates as Na^+ and Cl^- ions. Some water dissociates as H^+ and OH^- ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-, \qquad H_2O \rightleftharpoons H^+ + OH^-$$

On passing electric current hydrogen is liberated at the cathode and Cl_2 at the anode. The liberated Cl_2 reacts with the NaOH which is produced as a result of the electrolysis of NaCl solution to form sodium hypochlorite.

$$\begin{aligned} &\textit{At cathode} : 2H^+ + 2e = H_2\uparrow \\ &\textit{At anode} \;\;\; : 2Cl^- - 2e = Cl_2 \end{aligned}$$

$$Na^+ + OH^- \rightleftharpoons NaOH$$

$$NaOH + Cl_2 = NaCl + NaOCl + H_2O$$

Properties : (i) Sodium hypochlorite solution decomposes on heating to form *sodium chlorate* and *chloride*.

$$3NaOCl = NaClO_3 + 2NaCl$$

(ii) Action on acids : Dilute acids even the carbonic acid liberates hypochlorous acid from NaOCl.

$$NaOCl + H_2CO_3 = NaHCO_3 + HOCl$$

(iii) Oxidising property : As NaOCl gives off nascent oxygen it is a powerful oxidising agent.

(a) It can oxidise *arsenites* to *arsenate*.

$$Na_3AsO_3 + NaOCl = Na_3AsO_4 + NaCl$$

(b) Potassium iodide solution in presence of acids is oxidised to give free iodine.

$$2KI + NaOCl + 2HCl = I_2 + 2KCl + NaCl + H_2O$$

(c) Hydrochloric acid is oxidised to chlorine.

$$2HCl + NaOCl = H_2O + NaCl + Cl_2$$

Uses : It is used (i) as bleaching agent for paper, pulp, cotton, rayon, linen etc. ; (ii) as a disinfectant and deodorant in water supplies and diaries.

• Exercises •

1. What are halogens ? Why are they so called ?

2. State the diffculties encountered during the isolation of fluorine. How fluorine gas is prepared by removing these difficulties ? [*W.B.H.S. 87*]

3. (a) How did Moissan overcome the difficulties in the isolation of fluorine ?
(b) Describe Moissan's method of preparation of fluorine.
(c) Describe the reactions of fluorine with chlorine and I_2. [*W.B.H.S. 89*]

4. In what respect does fluorine differ from the other members of halogen family ? Describe the modern process of the preparation of fluorine.

5. Which halogen does not form any oxyacid ? Explain why it does not form oxyacids similar to other halogens. Does this halogen form any compound with oxygen ?

6. (a) Describe the laboratory method of preparation of chlorine. [*W.B.H.S. 88*]
(b) How would you prepare chlorine without heating ? Give the equation of the reaction. [*W.B.J.E. 89*]
(c) Which property is responsible for the bleaching action of Cl_2 ? [*W.B.J.E. 90*]

7. (a) Describe the preparation of chlorine on a large scale.
(b) How is bleaching powder manufactured ? What is meant by available chlorine ? [*Jt. Ent. 90*]

8. Describe how would you prepare bromine in the laboratory ? Give an account of the extraction of bromine from sea water. How and in what condition does Br_2 react with (a) SO_2, (b) P, (c) NaOH, (d) KI ?

9. What are the chief sources of iodine ? Describe the extraction of iodine from these sources.

10. (a) How would you distinguish between (i) chlorine (g) and $Br_2(g)$ (ii) Cl_2 (g) and I_2 ? [*W.B.J.E. 91*]
(b) Of two gas jars one contains bromine vapours and the other NO_2 gas. How can you detect by simple experiment which jar contains which gas ? [*W.B.J.E. 91*]
(c) Illustrate with equation the reducing action of I_2. [*W.B.H.S. 92*]

11. What happens when—

(i) Fluorine is passed through CCl_4
(ii) F_2 is passed through KI solution.
(iii) F_2 is treated with NaOH solution.
(iv) Conc. HCl is dropped on $KMnO_4$ crystals. [*W.B.H.S. '89*]
(v) Water is gradually added to a mixture of red P and I_2. [*W.B.H.S. '91*]
(vi) Iodine is allowed to react with sodium thiosulphate. [*W.B.H.S. '91*]
(vii) Chlorine is passed through HBr solution. [*W.B.H.S. '92*]
(viii) Chlorine is passed through hot and conc. NaOH solution. [*W.B.H.S. '88*]
(ix) Iodine is added to aqueous solution of potassium iodide. [*W.B.H.S. '88*]
(x) SO_2 is passed through iodine suspended in water. [*W.B.H.S. '88*]
(xi) Potassium chlorate is heated with iodine. [*W.B.H.S. '87*]
(xii) Chlorine is reacted with ammonia. [*H.S. (Trip.) '87*]
(xiii) Br_2 is added dropwise on a mixture of red P and water. [*W.B.H.S. '87*]
(xiv) Cl_2 is passed through an aqueous solution of SO_2. [*W.B.H.S. '84*]
(xv) H_2S is passed through a suspension of I_2 in water. [*W.B.H.S. '84*]

(xvi) Starch iodide paper is held in a gas jar full of Cl_2. *[W.B.H.S. '84]*
(xvii) I_2 is heated with conc. nitric acid.
(xviii) Calcium fluoride is heated with conc. H_2SO_4 in a glass vessel.
(xix) Sodium silicate is treated with hydrofluoric acid. *[H.S. '92]*
(xx) Iodine is treated with chlorine water. *[H.S. '93]*
(xxi) A solution of KI is treated with chlorine water and carbon disulphide.
(xxii) Chlorine gases bubbled through a solution of ferrous bromide. *[I.I.T. '86]*
(xxiii) Potassium bromide is treated with conc. H_2SO_4.
(xxiv) Sodium iodate is treated with $NaHSO_3$ solution. *[I.I.T. '82]*
(xxv) H_2S is passed through chlorine water. *[H.S. '83]*
(xxvi) Cl_2 is passed through cold and dilute NaOH solution. *[H.S. '78]*
(xxvii) CO_2 gas is passed through bleaching powder suspended in water.
(xxviii) Cl_2 is treated with sodium sulphite and HCl is treated with bleaching powder. *[I.I.T. '78]*
(xxix) KI is reacted with $FeCl_3$ solution. *[Jt. Ent. '78]*
(xxx) Fluorine is reacted with Cl_2 and Br_2 respectively. *[H.S. '89]*
(xxxi) H_2S passed through ferric chloride solution acidified with HCl. *[H.S. '93]*
(xxxii) NH_3 is reacted with chlorine. *[Jt. Ent. '92]*

12. How is anhydrous hydrofluoric acid prepared ? Distinguish between hydrogen fluoride and hydrofluoric acid. What do you mean by etching of glass ?

13. Describe the laboratory method of preparation of hydrogen chloride and hydrochloric acid.

14. Describe the laboratory method of preparation of hydrobromic acid and hydroiodic acid.

15. In the reactions $Cl_2 + 2KI = 2KCl + I_2$

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2$$

Explain why Cl_2 displaces I_2 from KI and I_2 displaces Cl_2 from $KClO_3$?

16. Compare the chemistry of hydrides, oxides, oxyacids of halogens. How would you justify the inclusion of fluorine, chlorine, bromine and iodine in the same group ?

17. There is a mixture of KF, KCl, KBr and KI. What oxidising agent would you use so that only I_2 liberates from KI without the liberation of any other halogens ? After the liberation of iodine, what oxidising agent would you use to liberate Br_2 only and then Cl_2 only. Can you oxidise the fluoride ? Explain your answer.

18. Explain why—

(i) Fluorine is the most active element.
(ii) Fluorine is called the super halogen.
(iii) Fluorine can not be prepared by the electrolysis of an aqueous solution of HF. *[H.S. '91] [Jt. Ent. '89]*
(iv) Fluorine is the strongest and iodine is the weakest oxidising agent. *[Roorke Eng. '87]*
(v) Fluorine exhibits only oxidation state of -1 while other halogens exhibit negative as well as positive oxidation states. *[H.S. '92]*
(vi) HF is weaker acid than HCl.
(vii) HBr cannot be prepared by the action of conc. H_2SO_4 on NaBr or KBr. *[H.S. '88] [J. Ent. '87]*
(viii) The gaseous mixture evolved by the action of fluorine with water gives a fishy smell. *[J. Ent. '90]*
(ix) HI is the strongest reducing agent of all halogen acids. *[J. Ent. '89]*
(x) Fluorine can not be prepared by the oxidation of fluoride salt. *[H.S. '88, J. Ent. '89]*
(xi) Chlorine can not bleach a dry substance.
(xii) Mark of lead pencil or printing ink cannot be bleached by Cl_2.
(xiii) HF is not kept in glass vessel.
(xiv) Reddish brown colour of bromine water is decolourised by the addition of NaOH.
(xv) A fresh stain of iodine is removed by washing with hypo solution.
(xvi) Chlorine is more powerful oxidising agent than Br_2 or I_2. *[Jt. Ent. '82]*
(xvii) Pure water and anhydrous HCl are non conductor of electricity but the aqueous solution of HCl can conduct electricity. *[Jt. Ent. '87]*
(xviii) Hydrogen chloride is a covalent compound but its aqueous solution can conduct electricity. *[I.I.T. '79]*
(xix) HI has the reducing power.
(xx) Blue litmus at first turns red and then becomes colourless when dipped in hypochlorous acid. *[I.I.T. '79, H.S. '89]*
(xxi) HI cannot be prepared by the action of conc. H_2SO_4 on NaI or KI. *[Jt. Ent. '81, H.S. '90]*
(xxii) I_2 is sparingly soluble in water but its solubility is much increased in aqueous solution of KI. *[Jt. Ent. '92, H.S. '82]*

(xxiii) Instead of conc. H_2SO_4, conc. HCl is used in the flame test for detection of basic radical. *[Jt. Ent. '87]*
(xxiv) H_3PO_4 is used for the preparation of HI from iodide salts instead of conc. H_2SO_4. *[I.I.T. '82]*
(xxv) HF is most stable and HI is the least stable among halogen acids.
(xxvi) The boiling point of HF is greater than that of HCl.
(xxvii) Conc. H_2SO_4 or CaO is unfit for drying HI or HBr.
(xxviii) The brown colour of the acidified solution of I_2 in KI solution is intensified by the addition of a nitrite, but is discharged by the addition of a sulphite.
(xxix) Bleaching powder loses its bleaching property when kept open in a bottle for a long time.
(xxx) The salt KHF_2 is well-known but $KHCl_2$ or $KHBr_2$ does not exist.
(xxxi) HF is a liquid while HCl, HBr or HI are gases.
(xxxii) Iodine behaves as a cation.
(xxxiii) Fluorine can not be oxidised by any oxidising agent.
(xxxiv) Fluorine can not form oxyacids.

19. How would you separate —
(a) HF from fluorine (b) HCl from Cl_2 (c) Cl_2 from bromine (d) Potassium iodide from I_2 (e) Moisture from HF (f) Bromine from HBr (g) HCl gas from CO_2 *[W.B.H.S. '89]*

20. How would you distinguish between —
(a) Chlorine and iodine *[Jt. Ent. '92]* (b) Chlorine and bromine *[Jt. Ent. '91]* (c) Fluorine and chlorine (d) Bromine and nitrogen dioxide *[Jt. Ent. '91]* (e) Iodine and bromine (f) Graphite and iodine (g) F^- and Cl^- (h) Br^- and I^- (i) Cl^- and I^-.

21. Prove that —
(a) HCl contains Cl_2 (b) HBr contains Br_2 (c) HI contains I_2 (d) KI contains I_2 (e) $KClO_3$ contains oxygen and Cl_2 (f) KBr contains Br_2 (g) NaCl contains Cl_2.

22. How would you bring out the following —
(a) Oxidation of KF (b) Oxidation of a chloride by MnO_2 (c) Preparation of I_2 from an iodide (d) Detection of Br^- and I^- ions in the mixture of the two (e) Preparation of hypochlorite from brine (f) Oxidation of oxygen (g) Etching of glass (h) Replacement of Cl_2 from a compound of chlorine by I_2 (i) A reaction where iodine acts as a cation (j) Reducing action of Br_2 and I_2 (k) Preparation of anhydrous HF *[W.B.H.S. '93]* (l) Preparation of Cl_2 from NaCl *[W.B.H.S. '93]*.

23. Prove that —
(a) HCl contains chlorine and HBr contains bromine. (b) Potassium chlorate contains chlorine and oxygen. (c) Chlorine is stronger oxidising agent than iodine. (d) HI is stronger reducing agent than HBr.

24. (a) A black substance may be either carbon or MnO_2. How will you proceed to identify them ?
(b) A solid may be graphite or iodine. How would you identify the solid ?
(c) How would you detect the presence of traces of Cl_2 in a sample of hydrogen chloride ?
(d) Explain the bleaching action of chlorine and compare it with that of sulphur dioxide. *[W.B.H.S. '88]*
(e) How would you separate the constituents of a mixture of potassium iodide and iodine ?
(f) O_2 is prepared by heating a mixture of $KClO_3$ and MnO_2 and Cl_2 is prepared by heating conc. HCl with MnO_2. What is the role of MnO_2 in these two different reactions.
(g) With the help of a chemical reaction show that iodine acts as an oxidising agent. *[W.B.H.S. '86]*
(h) How can a small quantity of Cl_2 mixed with O_2 be removed ? *[W.B.H.S. '86]*
(i) Show with the help of a chemical reaction that the reactivity gradually decreases from F_2 to I_2.

25. Choose the correct one —
(i) The outermost electronic configuration of the most electronegative element is—
(a) $ns^2 np^3$, (b) $ns^2 np^4$, (c) $ns^2 np^6$, (d) $ns^2 np^5$. **[Ans. (d)]** *[I.I.T. '88]*
(ii) Cl_2 acts as bleaching agent only in presence of—
(a) dry air, (b) sun light, (c) moisture, (d) pure O_2. **[Ans. (c)]** *[I.I.T. '83]*
(iii) Which of the halogens exhibits only one oxidation state ?—
(a) Cl_2, (b) Br_2, (c) I_2, (d) F_2. **[Ans. (d)]**
(iv) Iodine is dissolved in KI solution as—
(a) I^+ ion, (b) I^- ion, (c) I_3^- ion, (d) I_2^- ion. **[Ans. (c)]**
(v) Which of the following has the highest bond energy ?
(a) F—F, (b) Cl—Cl, (c) Br—Br, (d) I—I. **[Ans. (b)]**
(vi) Which of the following is most stable to heat ?
(a) HCl, (b) HOCl, (c) HBr, (d) HI. **[Ans. (a)]** *[I.I.T. '80]*
(vii) Which of the following is the weakest acid ?
(a) HF, (b) HBr, (c) HI, (d) HCl. **[Ans. (a)]** *[I.I.T. '80]*
(viii) HBr and HI reduce H_2SO_4, HCl can reduce $KMnO_4$ and HF can reduce—

(a) H_2SO_4, (b) $KMnO_4$, (c) $K_2Cr_2O_7$, (d) none of these. [Ans. (d)] *[I.I.T. '81]*
(ix) Br_2 can be liberated from KBr solution by the action of—
(a) I_2 soln., (b) Cl_2 water, (c) NaCl soln., (d) KI soln. [Ans. (b)] *[I.I.T. '87]*
(x) Which one of the following is the strongest acid ?—
(a) $ClO_3(OH)$, (b) $ClO_2(OH)$, (c) $SO(OH)_2$, (d) $SO_2(OH)_2$. [Ans. (a)] *[I.I.T. '89]*
(xi) Which of the following has the highest boiling point ?—
(a) HI, (b) HF, (c) HCl, (d) HBr. [Ans. (b)]
(xii) Which of the following does not form oxyacids ?—
(a) Cl_2, (b) Br_2, (c) I_2, (d) F_2. [Ans. (d)] *[AIMS '93]*
(xiii) When F_2 is passed through cold and dilute NaOH soln., we get —
(a) HI, (b) H_2F_2, (c) F_2O, (d) No reaction. [Ans. (c)] *[Orissa Jt. Ent. '89]*
(xiv) Low bond energy of F_2 molecule is best explained by its—
(a) high electronegativity, (b) small size, (c) attainment of noble gas configuration, (d) repulsion by lone pairs of fluorine atom. [Ans. (b)]
(xv) Which of the following is the strongest oxidising agent ?
(a) F_2, (b) Br_2, (c) I_2, (d) Cl_2. [Ans. (a)]
(xvi) Which one is the best covalent ?—
(a) $SnCl_2$, (b) $SnCl_4$, (c) SnF_2, (d) SnF_4, (e) $SiCl_4$. [Ans. (b)] *[Jt. Ent. '92]*

26. Fill up the gaps —
(i) The increase in solubility of I_2 in KI solution is due to formation of .... *[I.I.T. '82]*
(ii) When KBr is heated with conc. H_2SO_4 .... is (are) produced.
(iii) I_2 reacts with NaOH solution. The products are NaI and .... *[I.I.T. '90]*
(iv) Of all halogens .... exhibits positive oxidation state.
(v) Silver fluoride is .... in water. *[I.I.T. '82]*
(vi) I_2 displaces Cl_2 from ....

27. Arrange the following in the increasing order of —
(i) Stability — HF, HCl, HI, HBr
(ii) Thermal stability — HOCl, $HOClO_2$, $HOClO_3$, HOClO *[I.I.T. '88]*
(iii) Oxiding power — Cl_2, Br_2, I_2, F_2
(iv) Strength of acid — $HClO_4$, $HClO_3$, $HClO_2$ HClO
(v) Bond length — HF, HCl, HBr, HI

[illegible]

Fluorine can not [illegible]

19. How would you separate —

(a) HF from fluorine (b) HCl from [illegible] from HBr [illegible]

20. How would you distinguish between —

(a) Chlorine and iodine [illegible] (d) Bromine and nitrogen dioxide [illegible]

21. Prove that —

(a) HCl contains Cl_2 (b) HBr contains Br_2 (c) HI contains I_2 [illegible] oxygen and Cl_2 (f) KBr contains Br_2 (g) NaCl contains Cl_2.

22. How would you bring out the following —

(a) Oxidation of KF (b) Oxidation of a chloride [illegible] Detection of Br^- and I^- ions in the mixture [illegible] Oxidation of oxygen (g) Etching of glass (h) Bleaching [illegible] reaction where iodine acts as a cation (j) [illegible] *[W.B. H.S. '83]* (l) Preparation of Cl_2 from NaCl *[W.B.H.S. '93]*

23. Prove that —

(a) HCl contains chlorine and HBr contains bromine. (b) Potassium chlorate contains chlorine and oxygen. (c) Chlorine is stronger oxidising agent than iodine. (d) HI is stronger reducing agent than HBr.

24. (a) A black substance may be either [illegible] or MnO_2. How will you proceed to identify them ?

(b) A solid may be graphite or iodine. How would you identify the solid ?

(c) How would you detect the presence of traces of Cl_2 in a sample of hydrogen chloride ?

(d) Explain the bleaching action of chlorine and compare it with that of sulphur dioxide. *[W.B.H.S. [illegible]]*

(e) How would you separate the constituents of a mixture of potassium iodide and iodine ?

(f) O_2 is produced by heating a mixture of $KClO_3$ and MnO_2 and Cl_2 is prepared by heating conc. HCl with MnO_2. What is the role of MnO_2 in these two different reactions.

(g) With the help of a chemical reaction show that iodine acts as oxidising agent. *[W.B.H.S. '86]*

(h) How can a small quantity of Cl_2 mixed with O_2 be removed ? *[W.B.H.S. '89]*

(i) Show with the help of a chemical reaction that the reactivity gradually decreases from F_2 to I_2.

25. Choose the correct one —

(i) The outermost electronic configuration of the most electronegative element is —

(a) $ns^2\ np^3$, (b) $ns^2\ np^4$, (c) $ns^2\ np^5$, (d) $ns^2\ np^6$ [Ans. (c)] *[I.I.T. [illegible]]*

(ii) Cl_2 acts as bleaching agent only in presence of —

(a) dry air, (b) sunlight, (c) moisture, (d) pure O_2 [Ans. (c)] *[I.I.T. [illegible]]*

(iii) Which of the halogens exhibits only one oxidation state ? —

(a) Cl, (b) Br, (c) I, (d) F [Ans. (d)]

[illegible]

• APPENDIX •

If our students are acquainted with the types of questions which are generally set in the Joint Ent., I.I.T admission test and other competitive examinations on all India basis, they will face no difficulty in answering such types of questions. At present different types of short type questions are set in these examinations. The answers of such types of questions have already been discussed in different chapters of this book. For the convenience of the students some important questions are given here so that they can get a clear idea of such types of questions and their ideal answers at a glance.

[A] Name and give the formula of :

1. Two liquid dehydrating agents.

[*Ans :* Conc. sulphuric acid, H_2SO_4 and Conc. phosphoric acid, H_3PO_4]

2. Two metallic oxides which on heating evolve O_2 and are converted to the respective metals.

[*Ans :* Mercuric oxide, HgO and silver oxide Ag_2O]

3. Two nitrates which on heating give nitrites and evolve O_2.

[*Ans :* Sodium nitrate, $NaNO_3$ and potassium nitrate, KNO_3]

4. A compound and an element which have bleaching property.

[*Ans :* Compound-Sulphur dioxide, SO_2 and element-chlorine, Cl_2]

5. Two amphoteric oxides.

[*Ans :* Aluminium Al_2O_3 ; and zinc oxide, ZnO]

6. Two acidic metallic oxides.

[*Ans :* Manganese heptoxide, Mn_2O_7 ; $Mn_2O_7 + H_2O = 2HMnO_4$. Chronium tri oxide, CrO_3 ; $CrO_3 + 2KOH = K_2CrO_4 + H_2O$]

7. A compound, the solution of which on being heated gives a white precipitate with the evolution of a colourless gas.

[*Ans :* Calcium bicarbonate, $Ca(HCO_3)_2$, $Ca(HCO_3)_2 \xrightarrow[\Delta]{} CaCO_3\downarrow + CO_2\uparrow + H_2O$]

8. Two metals which react with strong alkali to produce hydrogen.

[*Ans :* Al and Zn. $2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2\uparrow$; $Zn + 2NaOH = Na_2ZnO_2 + H_2\uparrow$]

9. Two non metals which react with strong alkali to produce hydrogen.

[*Ans :* Boron and silicon. $2B + 2NaOH + 2H_2O = 2NaBO_2 + 3H_2\uparrow$; $Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$]

10. A metal which reacts with strong alkali to liberate a gas which burns with a bluish flame.

[*Ans :* See the answer of Q. 8]

11. A metal and a non metal which are liquid at ordinary temperature.

[*Ans :* metal—mercury Hg, non metal—bromine Br_2]

12. Two substances which are responsible for the hardness of water.

[*Ans :* Magnesium sulphate $MgSO_4$ and Calcium chloride $CaCl_2$]

13. A solid compound which is produced by the action of two colourless gases.

[*Ans :* Hydrogen chloride (HCl) and ammonia (NH_3). The solid compound is ammonium chloride NH_4Cl. $HCl(g) + NH_3(g) = NH_4Cl(s)$

14. Two solid dehydrating agents.

[*Ans :* Calcium oxide, CaO and phosphorus pentoxide (P_2O_5)]

15. A deliquescent and an efflorescent substance.

[*Ans :* deliquescent substance = magnesium chloride ($MgCl_2$) ; efflorescent substance—sodium carbonate Na_2CO_3 ; $10H_2O$]

16. An aqueous solution of a salt in which the solubility of iodine is high.

[*Ans :* Potassium iodide (KI). Solid iodine reacts with KI to form a complex potassium tri-iodide which is very soluble in water. $KI + I_2 = KI_3$]

17. Two gases which liberate iodine from KI.

[*Ans :* chlorine (Cl_2) and Ozone (O_3). $2KI + Cl_2 = 2KCl + I_2$, $2KI + O_3 + H_2O = 2KOH + I_2 + O_2$]

18. Two substances which liberate Cl_2 from HCl.

[*Ans :* Potassium permanganate ($KMnO_4$) and manganese dioxide (MnO_2).

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$
$$MnO_4 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.]$$

19. Two heat producing gases present in coal gas.

[*Ans :* Methane (CH_4) and hydrogen (H_2)]

20. An aqueous solution of a salt when $AgNO_3$ solution is added to it a white precipitate is obtained which is not soluble in HNO_3 but soluble in excess of NH_4OH.

[*Ans :* Sodium Chloride (NaCl) $NaCl + AgNO_3 = AgCl\downarrow + NaNO_3$]

21. An acid and a salt, the aqueous solution of which on being treated with $BaCl_2$ separately, yields white precipitate which is insoluble in HNO_3.

[*Ans :* Sulphuric acid (H_2SO_4) and sodium sulphate (Na_2SO_4)]

22. Two substances which produce temporary hardness of water.

[*Ans :* Calcium bicarbonate $Ca(HCO_3)_2$ and magnesium bicarbonate $Mg(HCO_3)_2$]

23. An element and a compound which bleach by oxidation.

[*Ans :* Element—chlorine, compound—hydrogen peroxide (H_2O_2)]

24. A peroxide which has both oxidising and reducing properties.

[*Ans :* Hydrogen peroxide—H_2O_2, Oxidising property— $Pb\overset{-2}{S} + 4H_2O_2 = Pb\overset{+6}{S}O_4 + 4H_2O$; reducing property— $2K\overset{+7}{Mn}O_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 5O_2 + 8H_2O$]

25. A compound in which the valency (oxidation No.) of iron is +6.

[*Ans :* Potassium ferrate ($K_2\overset{+6}{Fe}O_4$)]

26. A double salt in which iron is present.

[*Ans :* Mohr's salt $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$]

27. A complex salt in which iron is present.

[*Ans :* Potassium ferro cyanide $K_4[Fe(CN)_6]$]

28. A Complex salt in which NH_3 is present.

[*Ans :* Cupro ammonium sulphate $[Cu(NH_3)_4]\,SO_4$]

29. A compound in which NO is present.

[*Ans :* Nitrosoferrous sulphate $Fe(NO)SO_4$]

30. An oxide which is a supporter of combustions.

[*Ans :* Nitrous oxide (N_2O)]

31. A gas which is absorbed in alkaline pyrogallate.

[*Ans :* Oxygen.]

32. A gas which is absorbed in terpentine.

[*Ans :* Ozone O_3]

33. A gas which is absorbed in aqueous ferrous sulphate solutions.

[*Ans :* Nitric oxide (NO)]

34. An element which can not be oxidised.

[*Ans :* Fluorine F_2]

35. A gas, which being treated with water evolves a gas having fishy smell.

[*Ans :* Fluorine $3H_2O + 3F_2 = 6HF + O_3\uparrow$]

36. Two metals which evolve H_2 by reacting with dil. HNO_3.

[*Ans :* Mg and Mn.]

37. A non metal which conducts electricity.

[*Ans :* Graphite C]

38. A salt which does not hydrolyse.

[*Ans :* Sodium chloride $NaCl$]

39. Two acids which have both oxidising and reducing power.

[*Ans :* Nitrous acid (HNO_2) and sulphurous acid (H_2SO_3)]

40. A mixed oxide and a super oxide.

[*Ans :* Mixed oxide—feroso ferric oxide (Fe_3O_4), super oxide—potassium super oxide (KO_2)]

41. A non metal, which on being treated with hot NaOH evolves a gas having the smell of rotten egg.

[*Ans :* White phosphorus P_4. phosphine is evolved which has the smell of rotten egg. $P_4 + 3NaOH + 3H_2O = PH_3\uparrow + 3NaH_2PO_2$]

42. A fertiliser having N_2 and Ca.

[*Ans :* Nitrolim ($CaCN_2 + C$)]

43. A fertiliser having NH_3.

[*Ans :* Ammonium sulphate $(NH_4)_2SO_4$]

44. A salt which is isomorphous with $NaNO_3$.

[*Ans :* Sodium iodate ($NaIO_3$)]

45. A white solid which on being heated liberates a colourless gas and the colour of the residue becomes yellow while hot and white when cold.

[*Ans :* Zinc carbonate ($ZnCO_3$). $ZnCO_3 \xrightarrow[\Delta]{} ZnO + CO_2\uparrow$

46. A substance by which diamond can be cut.

[*Ans :* Boron carbide (B_4C)]

47. An oxide which produces H_2O_2 and O_2 by its action with an acid.

[*Ans :* Potassium super oxide (KO_2) $2KO_2 + 2HCl = 2KCl + H_2O_2 + O_2$]

48. A reaction in which O_2 acts as a reducing agent.

[*Ans :* $2\overset{0}{F}_2 + O_2 + 2\overset{-1}{F}_2O$]

49. A sodium salt, to an aqueous solution of which sodium nitroprusside soln. being added, turns violet.

[*Ans :* Sodium sulphide (Na_2S).

$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$

50. A reaction, where H_2 acts as an oxidising agent.

[*Ans :* $2Na + \overset{0}{H}_2 = 2Na\overset{-1}{H}$]

51. A metal as a part of an anion.

[*Ans :* In potassium permanganate, Mn is present as permanganate ion. $KMnO_4 \rightleftharpoons K^+ + MnO^-_4$]

52. A catalyst used in the synthesis of NH_3 from elements.

[*Ans :* Iron powder is used as catalyst in the synthesis of ammonia from N_2 and H_2]

53. A salt, which on being heated, evolves a colourless gas leaving a residue which is reddish brown while hot and yellow when cold.

[*Ans :* Lead carbonate ($PbCO_3$). $PbCO_3 = PbO + CO_2$; Colour of PbO is reddish brown when hot and yellow when cold]

54. A salt which on heating evolves brown gas. [*Ans :* Lead nitrate $Pb(NO_3)_2$, the brown gas is NO_2. $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$]

55. A compound in which the oxidation number of oxygen is + 2.

[*Ans :* Fluorine monoxide F_2O.]

56. A carbide which gives acetylene when treated with water.

[*Ans :* Calcium carbide CaC_2]

57. A phosphide which gives phosphine when treated with water.

[*Ans :* Ca_3P_2 calcium phosphide $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$].

58. A compound of nitrogen which gives NH_3 on being treated with water.

[*Ans :* Magnesium nitride (Mg_3N_2) $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$].

59. An oxide which gives an oxyacid on being treated with water.

[*Ans* : Carbon dioxide(CO_2) $CO_2 + H_2O = H_2CO_3$].

60. A compound of boron which swells up on heating.

[*Ans* : Borax, $Na_2B_4O_7, 10H_2O$].

61. A chloride which gives HCl with water.

[*Ans* : Ferric chloride ($FeCl_3$). $FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl$

62. A hardest substance.

[*Ans* : Boron carbide (B_4C)]

63. A gas which is isoelectronic with CO.

[*Ans* : Nitrogen (N_2)]

[B] How would you remove:

1. Cl_2 and CO_2 from oxygen.

[*Ans* : The gas mixture is passed through NaOH soln. when Cl_2 reacts with NaOH to form NaCl and $NaClO_3$. CO_2 reacts with NaOH to form Na_2CO_3. The unreacted O_2 passes out and collected.

$6NaOH + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O$.

$CO_2 + 2NaOH = Na_2CO_3 + H_2O$

2. Nitrous oxide from oxygen.

[*Ans* : The gas mixture is passed through ethanol when N_2O is absorbed in it and O_2 passes out and is collected.]

3. NO_2 from oxygen.

[*Ans* : The gas mixture is passed through a freezing mixture when NO_2 is condensed to form a yellow liquid and O_2 passes out.]

4. SO_2 from oxygen.

[*Ans* : The gas mixture is passed through NaOH soln. when SO_2 reacts with it to form Na_2SO_3 and unreacted O_2 passes out. $SO_2 + 2NaOH = Na_2SO_3 + H_2O$].

5. PH_3 and H_2S from hydrogen.

[*Ans* : H_2S is removed by passing the gas mixture through lead nitrate solution and then the gas mixture is passed through $AgNO_3$ soln. when PH_3 is removed. H_2 passes out and is collected.

$H_2S + Pb(NO_3)_2 = PbS\downarrow + 2HNO_3$

$PH_3 + 6AgNO_3 = Ag_3P, 3AgNO_3\downarrow + 3HNO_3$].

6. CO_2 and SO_2 from hydrogen.

[*Ans* : The gas mixture is passed through NaOH solution when CO_2 reacts with NaOH to form Na_2CO_3 and SO_2 reacts with NaOH to form Na_2SO_3. H_2 passes out.

$2NaOH + CO_2 = Na_2CO_3 + H_2O$; $2NaOH + SO_2 = Na_2SO_3 + H_2O$.]

7. Phosphine and N_2 from H_2.

[*Ans* : See purification of hydrogen, Page-20 Inorganic]

8. Oxygen from hydrogen.

[*Ans* : The gas mixture is passed through alkaline pyrogallate soln. when O_2 is absorbed and H_2 passes out.]

9. Water from hydrogen peroxide.

[*Ans* : See purification of hydrogen peroxide, page-60, Inorganic]

10. Oxygen from Ozone.

[*Ans* : See purification of O_3 page-74, Inorganic]

11. Ozone from oxygen.

[*Ans* : The gas mixture is passed through terpentine when O_3 is absorbed and O_2 passes out.]

12. Moisture from ammonia.

[*Ans* : See purification of ammonia, Page-100, Inorganic]

13. O_2 from ammonia.

[*Ans* : The gas mixture is passed through HCl when NH_3 reacts with HCl to form NH_4Cl and oxygen passes out. The NH_4Cl thus obtained is heated with NaOH when NH_3 recovered.

$NH_3 + HCl = NH_4Cl$; $NaOH + NH_4Cl = NH_3\uparrow + NaCl + H_2O$

14. Nitrogen from ammonia.

[*Ans :* The gas mixture is passed through HCl when NH_3 reacts with it to form NH_4Cl and N_2 passes out. The NH_4Cl thus formed when heated with NaOH gives NH_3.]

15. Ammonia from nitrogen.

[*Ans :* NH_3 is removed by passing the gas mixture through HCl soln.]

16. Cl_2 from nitrogen.

[*Ans :* Cl_2 is removed by passing the gas mixture through NaOH soln. When Cl_2 reacts with NaOH to form NaCl and $NaClO_3$. N_2 passes out and is collected.
$6NaOH + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O$.]

17. Nitric oxide from nitrous oxide.

[*Ans :* The gas mixture is passed through $FeSO_4$ solution when NO reacts with $FeSO_4$ to form a precipitate of a complex and N_2O passes out. $FeSO_4 + NO + 5H_2O = [Fe(H_2O)_5NO]SO_4$

18. Nitrogen di-oxide from nitrous oxide.

[*Ans :* The gas mixture is passed through NaOH solution when NO_2 being acidic oxide reacts to form $NaNO_2$ and $NaNO_3$. N_2O being neutral oxide passes out.
$2NaOH + 2NO_2 = NaNO_2 + NaNO_3 + H_2O$]

19. Ammonia from N_2O.

[*Ans :* The gas mixture is passed through HCl when NH_3 combines with HCl to form NH_4Cl. N_2O passes out. NH_3 is recovered from NH_4Cl as described in (13)]

20. N_2 from nitric oxide.

[*Ans :* The gas mixture is passed through $FeSO_4$ solution when NO is absorbed in it to form a complex (See Q. 17) and N_2 passes out and is collected.]

21. NO_2 from nitric acid.

[*Ans :* See purification of HNO_3. Page-124 inorganic]

22. SO_2 from CO_2.

[*Ans :* The gas mixture is passed through acidified $K_2Cr_2O_7$ soln. when CO_2 passes out without reaction but SO_2 is oxidised by $K_2Cr_2O_7$ to H_2SO_4]

23. Hydrogen chloride from CO_2.

[*Ans :* See Page-174 inorganic]—purification of CO_2]

24. Carbon monoxide from CO_2. .

[*Ans :* The gas mixture is passed through lime water when CO_2 reacts with lime water to form a white precipitate of $CaCO_3$ and CO being neutral oxide passes out. The $CaCO_3$ thus formed being treated with HCl gives CO_2. $Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$, $CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$]

25. CO_2 from CO.

[*Ans :* Same method as above]

26. NO from carbon monoxide.

[*Ans :* The gas mixture is passed through $FeSO_4$ soln. when NO reacts with $FeSO_4$ to form a complex and is precipitated. CO passes out and is collected. $FeSO_4 + NO + 5H_2O = [Fe(H_2O)_5NO]SO_4$

27. CO_2 from N_2.

[*Ans :* The gas mixture is passed through lime water when CO_2 is absorbed in it with the formation of $CaCO_3$, and N_2 passes out and is collected.]

28. Red P from white P and vice-versa.

[*Ans :* See purification of red P. Page-195 and preparation of white P from red P. page-196 inorganic.]

29. Phosphorus dihydride from Phosphine.

[*Ans :* See the purification of phosphine Page-202]

30. SO_3 from SO_2.

[*Ans :* The gas mixture is passed through NaOH solution when SO_2 reacts with NaOH to form Na_2SO_3 and SO_3 reacts to form Na_2SO_4. $2NaOH + SO_2 = Na_2SO_3 + H_2O$; $2NaOH + SO_3 = Na_2SO_4 + H_2O$.

A mixture of Na_2SO_4 and Na_2SO_3 thus obtained is then treated with dil HCl when Na_2SO_4 does not reacts with HCl but Na_2SO_3 reacts with HCl with the evolution of SO_2 [$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O$.]

31. CO_2 from SO_2. [*Ans :* The gas mixture is passed through Conc. HNO_3 when SO_2 is oxidised to form H_2SO_4. CO_2 being unreacted passes out with the produced NO_2. H_2SO_4 thus obtained is reacted with Cu when SO_2 is obtained.

$$SO_2 + 2HNO_3 = H_2SO_4 + NO_2\uparrow$$
$$Cu + 2H_2SO_4 = CuSO_4 + SO_2\uparrow + 2H_2O$$

32. Moisture from H_2S. [*Ans :* See the purification of H_2S. page-236 inorganic]

33. Hydrogen chloride from H_2S. [*Ans :* See the purification of H_2S. page-236 inorganic]

34. Hydrogen fluoride from fluorine. [*Ans :* See Page-282 purification of F_2]

35. Moisture and HCl from Cl_2. [*Ans :* See the purification of Cl_2 page-287]

36. Moisture and HBr from Br_2.

[*Ans :* The mixture is passed over $CaCl_2$ when moisture is removed. The mixture is then heated with MnO_2 when HBr is oxidised to form Br_2. $4HBr + MnO_2 = MnBr_2 + Br_2 + 2H_2O$]

37. Br_2 vapour from hydrogen bromide.

[*Ans :* The gas mixture is passed over glass beads coated with red P. Br_2 reacts with red P to form PBr_3. Hydrogen bromide passes out and is collected. $4P + 6Br_2 = 4P\,Br_3$]

38. Iodine vapour from hydrogen iodide.

[*Ans :* The gas mixture is passed over glass beads coated with red phosphorus when I_2 reacts with red P to form PI_3. Hydrogen iodide passes out. $4P + 6I_2 = 4PI_3$]

39. Cl_2 from HCl. [*Ans :* See the above process]

40. KBr or KI from KCl.

[*Ans :* Cl_2 is passed through the aqueous solution of the mixture of the salts when KBr or KI will be converted to KCl. $2KBr + Cl_2 = 2KCl + Br_2$; $2KI + Cl_2 = 2KCl + I_2$]

41. KCl from KBr.

[*Ans :* Cl_2 is passed through the aqueous solution of the mixture of two salts when KBr is converted to KCl and Br_2 is liberated. The Br_2 thus obtained is reacted with red phosphorus when PBr_3 is formed which is hydrolysed by water to form HBr. The produced HBr is then reacted with KOH when KBr is obtained.

$KBr + Cl_2 = KCl + Br_2$; $3Br_2 + 2P = 2PBr_3$.
$PBr_3 + 3H_2O = 3HBr + H_3PO_3$; $HBr + KOH = KBr + H_2O$.

42. Br_2 from Cl_2.

[*Ans :* KBr is added to the gas mixture and distilled when Cl_2 reacts with KBr to form KCl and Br_2 passes out. The KCl thus obtained is reacted with MnO_2 and Conc H_2SO_4 when Cl_2 is liberated]

[C] How could you prepare :

1. Oxygen from bleaching powder. [*Ans :* See page-7 inorg. chem.]

2. O_2 from oxide of heavy metals. [*Ans :* See page-4 inorg. chem.]

3. O_2 by the decomposition of an oxyacid. [*Ans :* See page-6 inorg. chem.]

4. Hydrogen by the reaction of a metal with steam. [*Ans :* See page-23 inorg. chem.]

5. Hydrogen by the reaction of a metal or a non metal with alkali.

[*Ans :* See page-23]

6. O_2 from lead nitrate. [*Ans :* See page-5 inorg. chem.]

7. H_2 from metallic hydride. [*Ans :* See page-24]

8. H_2O_2 from a peroxide. [*Ans :* See page-62]

9. H_2O_2 from a super oxide. [*Ans :* See page-199 phy. chem.]

10. Ammonia and nitrogen from sodium nitrite. [*Ans :* See page-92, N_2 thus produced is passed over heated Mg when Mg_3N_2 is produced which on being hydrolysed yields NH_3]

11. N_2 from ammonium dichromate. [*Ans :* See page-93]

12. N_2 from ammonia. [*Ans :* See page-94]

13. N_2 from nitric acid. [*Ans :* $2HNO_3 + 5Cu = 5CuO + N_2 + H_2O$]

14. N_2 from the oxides of nitrogen. [*Ans :* By passing the oxides of nitrogen over heated Cu.

$N_2O + Cu = CuO + N_2$; $2NO + 2Cu = 2CuO + N_2$

15. NH_3 from calcium cyanamide.

[*Ans :* Ammonia is liberated when calcium cyanamide is decomposed by super heated steam.
$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$]

16. H_2 from ammonia. [*Ans :* See page-103]

17. Laughing gas from HNO_3. [*Ans :* See page-112]

18. Nitrous oxide from NO. [***Ans :*** By reducing moist NO by SO_2 nitrous oxide is obtained.]
$2NO + SO_2 + H_2O = H_2SO_4 + N_2O$.

19. NO from ammonia.

[***Ans :*** The mixture of NH_3 and O_2 is passed over Pt wire gauze at 700°C. $4NH_3 + 5O_2 = 4NO + 6H_2O$]

20. NO and N_2O from a nitrate salt.

[***Ans :*** (i) $KNO_3 + NH_4Cl = KCl + NH_4NO_3$; $NH_4NO_3 \overset{\triangle}{\rightarrow} N_2O + 2H_2O$

(ii) $KNO_3 + \underset{\text{Conc.}}{H_2SO_4} \underset{200°C}{\overset{\triangle}{\rightarrow}} KHSO_4 + HNO_3$

$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 2NO + 4H_2O$

21. Ammonia from nitric oxide.

[***Ans :*** NH_3 is produced by reducing NO by hydrogen in presence of hot platinum catalyst.
$2NO + 5H_2 = 2NH_3 + 2H_2O$

22. Oxygen at ordinary temperature. [***Ans :*** See page-7]

23. Oxygen from barium oxide. [***Ans :*** See page-8]

24. Hydrogen from nitric acid. [***Ans :*** See page-129, action of Mg on HNO_3]

25. Nitric acid from ammonia. [***Ans :*** See page-107]

26. Nitric acid from nitrous acid. [***Ans :*** See page-122]

27. Boron from boron trioxide. [***Ans :*** See page-144]

28. Boron from ortho boric acid. [***Ans :*** See page-148]

29. Boron and boric acid from borax. [***Ans :*** See page-148]

30. Carbon monoxide from potassium ferrocyanide. [***Ans :*** See page-170]

31. CO from oxalic acid. [***Ans :*** See page-169]

32. CO from sodium formate. [***Ans :*** See page-170]

33. CO from carbon dioxide. [***Ans :*** See page-170]

34. CO_2 and CO from calcium carbonate (Marble) and sodium carbonate.

[***Ans :*** CO_2 is obtained by heating $CaCO_3$ at 900°C. $CaCO_3 = CaO + CO_2$, The produced CO_2 is passed over red hot Coke when CO_2 is reduced to form CO.

$CO_2 + C \xrightarrow{1400°C} 2CO$.

Na_2CO_3 is reacted with dil H_2SO_4 when CO_2 is liberated. The CO_2 thus obtained is reduced to CO by passing it over red hot coke.]

35. CO_2 from water gas. [***Ans :*** See page-176]

36. Urea from ammonia. [***Ans :*** See page-107]

37. N_2 and NH_3 from urea.

[***Ans :*** Preparation of N_2 from urea see page-94 The N_2 thus obtained is passed over heated Mg when Mg_3N_2 is produced. Mg_3N_2 is then treated with boiling water when NH_3 is produced $3Mg + N_2 = Mg_3N_2$;
$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3\uparrow$]

38. NH_3 from nitric acid.

[***Ans :*** HNO_3 is treated with NaOH when $NaNO_3$ is obtained. $HNO_3 + NaOH = NaNO_3 + H_2O$. $NaNO_3$ thus obtained is the reacted with Conc NaOH and metallic Zn powder when NH_3 is produced.
$NaNO_3 + 7NaOH + 4Zn = 4Na_2ZnO_2 + NH_3 + 2H_2O$]

39. N_2 from a nitride and P from a phosphide.

[***Ans :*** Nitride salt on being treated with boiling water gives NH_3. The produced NH_3 is then passed over heated CuO when N_2 is obtained. $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$; $3CuO + 2NH_3 = 3Cu + N_2 + 3H_2O$.
Phosphide on being treated with boiling water yields PH_3. $Cu_3P_2 + 6H_2O = 3Cu(OH)_2 + 2PH_3$. P from PH_3—see page-205]

40. Phosphine from phosphorus acid. [***Ans :*** $4H_3PO_3 \xrightarrow{\text{heated}} PH_3 + 3H_3PO_4$]

41. H_3PO_4 from bone ash. [***Ans :*** See page-192]

42. Sulphur dioxide without the application of heat. [***Ans :*** See page-244]

43. Ammonium sulphate from ammonia without H_2SO_4. [***Ans :*** See page-107]

44. H_2S and S from sodium sulphate.

[***Ans :*** Na_2SO_4 is mixed with Coke and the mixture is heated to 1000°C when Na_2SO_4 is reduced to Na_2S.

The produced Na_2S is then treated with dil HCl when H_2S is liberated. $Na_2SO_4 + 4C = Na_2S + 4CO\uparrow$; $Na_2S + 2HCl = 2NaCl + H_2S\uparrow$. The produced H_2S is passed through chlorine water when sulphur is precipitated. $H_2S + Cl_2 = 2HCl + S\downarrow$]

45. Sulphur from H_2S. [*Ans :* See page-239]

46. H_2S from S.

[*Ans :* A mixture of H_2 and vapour of S is passed through Ni-catalyst at 450°C when S combines with H_2 to form H_2S

$$H_2 + \xrightarrow[\text{Ni Cat}]{450} H_2S.$$

47. Rhombic sulphur from monoclinic sulphur and vice-versa. [*Ans :* See page-229]

48. White phosphorus, red phosphorus, phosphorus acid and phosphoric acid from calcium phosphate or phosphorite.

[*Ans :* White P ; See page-193 ; Red P- See page-195 ; H_3PO_3 Red P produced from calcium phosphate is treated with Cl_2 when PCl_3 is obtained. PCl_3 on hydrolysis yields H_3PO_3. (Red) $2P + 3Cl_2 = 2PCl_3$; $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$; H_3PO_4 See page-216]

49. Ozone from water.

[*Ans :* Ozone is obtained by the reactions of fluorine with water. $3H_2O + 3F_2 = 6HF + O_3$]

50. HI from I_2 and HBr from Br_2.

[*Ans :* When H_2S is passed through a suspension of I_2 in water I_2 is reduced to form HI. $H_2S + I_2 = 2HI + S\downarrow$. HBr can be prepared by the same process. $H_2S + Br_2 = 2HBr + S$.]

51. Sodium formate from CO_2.

[*Ans :* CO_2 is passed through coke at 1000°C when it is reduced to form CO. From CO to HCOONa—see page-171]

52. Metallic lead and N_2 from lead nitrate.

[*Ans :* Powdered $(Pb(NO_3)_2$ is kept in the cavity of a charcoal block and is heated with a blow pipe in the reducing flame when $Pb(NO_3)_2$ is at first converted to PbO. The produced PbO is then reduced by fine particles of carbon of the flame to produce metallic lead. $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$; $PbO + C = Pb + CO\uparrow$. The produced NO_2 is passed over heated Cu turnings when NO_2 is reduced to form N_2.

$2NO_2 + 4Cu = 4CuO + N_2$]

53. Anhydrous HF from CaF_2. [*Ans :* See page-309]

54. Phosphine from CaO and Phosphorus.

[*Ans :* CaO is treated with water when $Ca(OH)_2$ is produced. The produced $Ca(OH)_2$ is then heated with white P when phosphine is produced. $CaO + H_2O = Ca(OH)_2$; $3Ca(OH)_2 + 2P_4 + 6H_2O = 2PH_3$ $3Ca(H_2PO_2)_2$]

55. Nitric oxide from nitrogen dioxide.

[*Ans :* NO_2 is treated with hot water when HNO_3 and NO is produced. The produced NO passes out.

$3NO_2 + H_2O = 2HNO_3 + NO\uparrow$]

[D] Prove that :

1. Potassium chlorate contains Cl_2 and O_2.

[*Ans :* $KClO_3$ is taken in a hard glass test tube and is heated to 630°C when a colourless gas evolves which is absorbed in alkaline pyrogallate soln. turning it brown. A glowing splinter when introduced into the gas, it burns brilliantly. This proves that the gas is O_2 which comes from potassium chlorate. $2KClO_3 = 2KCl + 3O_2\uparrow$. The residue left in the test tube is mixed with MnO_2 and Conc H_2SO_4 is added to it and the mixture is heated, when a greenish yellow gas having the smell of bleaching powder is found to evolve. The gas turns starch iodide paper blue which proves that the gas is Cl_2 and this Cl_2 comes from potassium chlorate.

$2KCl + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + Cl_2\uparrow + 2H_2O$]

2. Bleaching powder contains O_2. [*Ans :* See page-332]

3. Potassium nitrate or sodium nitrate contains nitrogen and O_2. [*Hints :* $2KNO_3 = 2KNO_2 + O_2\uparrow$; $KNO_3 + NH_4Cl = NH_4NO_3 + KCl$; $NH_4NO_3 = N_2O + 2H_2O$; $N_2O + Cu = CuO + N_2$.]

4. Nitric acid contains N_2, O_2 and H_2. [*Ans :* See page-133]

5. Sulphuric acid contains S, O_2 and H_2. [*Ans :* See page-268]

6. Ammonia contains N_2 and H_2. [*Ans :* See page-106]

7. Carbon monoxide and carbon dioxide contains carbon. [*Ans* : See page-172, 179]

8. Phosphoric acid contains phosphorus. [*Ans* : See page-218]

9. Phosphorus acid contains phosphorus. [*Ans* : See page-218]

10. Phosphine contains P. [*Ans* : See page-205]

11. Phosphorite or calcium phosphite contains P. [*Ans* : See page-193]

12. Calcium fluoride contains fluorine.

[*Ans* : Calcium fluoride is mixed with conc. H_2SO_4 and the mixture is heated when HF is distilled out. The distillate is collected and reacted with KOH when KHF_2 is obtained. $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$; $2HF + KOH = KHF_2 + H_2O$. Ahydrous KHF_2 is mixed with HF and the mixture is electrolysed when a gas is found to evolve at the anode which reacts with water to form O_3 which is identified by its fishy smell.

$KHF_2 \rightleftharpoons KF + HF$; $KF \rightleftharpoons K^+ + F^-$. at anode : $2F^- + 2e = F_2$, $3H_2O + 3F_2 = 6HF + O_3 \uparrow$]

13. P_2O_3 contains P.

[*Ans* : P_2O_3 is treated with water when phosphorus acid is produced. $P_2O_3 + 3H_2O = 2H_3PO_3$. H_3PO_3 contains P—See page-218]

14. Hydrogen sulphide contains H_2 and S. [*Ans* : See page-242]

15. Sulphur dioxide contains S. [*Ans* : See page-249]

16. Nitric oxide or nitrogen dioxide or nitrous oxide contains nitrogen.

[*Ans* : The oxides of nitrogen (N_2O, NO, NO_2) when passed over heated Cu turnings are reduced to give a colourless gas which on being passed over heated Mg yields a white substance. This white substance on treatment with boiling water yields a gas having pungent odour which proves that the gas is NH_3 and the white powder is magnesium nitride which is produced by the action of the colourless gas on Mg. Thus it is proved that the gas is N_2.

$N_2O + Cu = CuO + N_2$; $3Mg + N_2 = Mg_3N_2$ $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3 \uparrow$]

17. Copper sulphate contains Cu.

[*Ans* : Fe powder is added to the aqueous solution of $CuSO_4$ when a red precipitate is obtained. The precipitate is dissolved in HNO_3 and the solution thus obtained is treated with excess of NH_4OH when a deep blue solution of cuproammonium nitrate is obtained. This proves the presence of copper.

$CuSO_4 + Fe = FeSO_4 + Cu \downarrow$; $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 2H_2O$

$2Cu(NO_3)_2 + 2NH_4OH = Cu(OH)_2, Cu(NO_3)_2 + 2NH_4NO_3$

$Cu(OH)_2, Cu(NO_3)_2 + 2NH_4NO_3 + 6NH_4OH = 2[Cu(NH_3)_4](NO_3)_2 + 8H_2O$]

18. Sodium sulphate or sulphide contains sulphur.

[*Ans* : Sodium sulphate is heated on a charcoal block in a reducing flame with a blow pipe when sodium sulphate is reduced by the carbon particles of the flame to produce sodium sulphide, sodium sulphide is then treated with dil HCl when H_2S gas is liberated. This H_2S when passed through chlorine water a yellow precipitate is obtained which burns in air to form a gas which decolourises the pink colour of acidified $KMnO_4$. Thus it is proved that the gas is SO_2 which is formed by the combustion of the yellow precipitate. So the precipitate is nothing but sulphur.

$Na_2SO_4 + 4C = Na_2S + 4CO \uparrow$; $Na_2S + 2HCl = 2NaCl + H_2S$

$H_2S + Cl_2 = 2HCl + S \downarrow$; $S + O_2 = SO_2 \uparrow$

19. Hydrogen chloride contains chlorine and hydrogen. [*Ans* : See page-317]

20. Hydrogen bromide contains bromine. [*Ans* : See page-322]

21. Potassium iodide contains I_2. [*Ans* : Cl_2 is passed through an aqueous solution of KI when brown substance is liberated which turns starch blue. So the brown substance is iodine.

$2KI + Cl_2 = 2KCl + I_2$; Starch + $I_2 \rightarrow$ turns blue.

22. HI contains I_2. [*Ans* : See page-327]

23. Ozone and oxygen are the allotropes of the same element. [*Ans* : See page-79]

24. Ammonia can be obtained from nitrate and nitrites. [*Ans* : See page-101]

25. HNO_3 is a strong oxidising agent. [*Ans* : See page-134]

26. Calcium sulphite contains sulphur. [*Ans* : Calcium sulphite is treated with dil HCl and the gas produced is dissolved in water. The aqueous solution of the gas is taken in a glass bulb is heated to 150°C when a yellow precipitate is obtained. The precipitate is collected which is found to be soluble in CS_2 and when it is burnt in air, produces a pungent smelling gas which decolourises acidified $KMnO_4$ solution. Thus it is proved that the gas is SO_2 which is obtained by the combustion of the yellow precipitate. So the yellow ppt is sulphur. This S has come from calcium sulphite.

$CaSO_3 + 2HCl = CaCl_2 + SO_2 + H_2O$

$SO_2 + H_2O = H_2SO_3$; $3H_2SO_3 = 2H_2SO_4 + S + H_2O$

[E] Show that—

1. Nascent hydrogen is more strong reducing agent than ordinary hydrogen. [*Ans* : See page-30]
2. H_2O_2 has both the oxidising and reducing property. [*Ans* : See page-67]
3. SO_2 has both the oxidising and reducing properties. [*Ans* : See page-247]
4. H_2O_2 behaves as an acid. [*Ans* : See page-64]
5. Both CO and SO_2 can form additive compounds. [*Ans* : See page-171 and 249]
6. H_3PO_3 has reducing property. [*Ans* : See page-214]
7. SiO_2 is an acidic oxide. [*Ans* : Silica is an acidic oxide as it reacts with base and forms salts. Thus Silica reacts with NaOH and is converted to sodium silicate. $SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$]
8. Air is a mechanical mixture. [*Ans* : See page-90]
9. PH_3 is alkaline. [*Ans* : See page-204]
10. NH_3 has reducing property. [*Ans* : See page-103]
11. I_2 has both the oxidising and reducing properties. [*Ans* : See page-304]
12. H_2O_2 can produce additive compounds. [*Ans* : See page-68]
13. H_2 can act as an oxidising agent. [*Ans* : See page-27]
14. SO_2 can form additive compounds. [*Ans* : See page-249]
15. O_3 is stronger oxidising agent than oxygen. [*Ans* : See page-86]
16. White P and red P are the allotropics of the same element. [*Ans* : See page-200]
17. HNO_2 has both oxidising and reducing properties. [*Ans* : See page-122]
18. Br_2 is stronger oxidising agent than I_2. [*Ans* : See page-299(iv)]
19. In some cases I_2 can replace Cl_2 from its compounds. [*Ans* : See page-303(8)]
20. O_2 can act as reducing agent. [*Ans* : See page-11]

[F] State one chemical reaction in each case by which you can distinguish between the following pairs of compounds.

1. Oxygen and nitrous oxide. [*Ans* : See page-113]
2. Oxygen and ozone. [*Ans* : See page-80]
3. H_2O_2 and O_3. [*Ans* : See page-81]
4. H_2O_2 and H_2O. [*Ans* : See page-81]
5. CO_2 and SO_2. [*Ans* : See page-250]
6. CO and CO_2. [*Ans* : See page-182]
7. H_2 and CO. [*Ans* : Both the gases burns with a bluish flame but during burning, H_2 combines with O_2 to form H_2O which turns anhydrous $CuSO_4$ (white) blue $2H_2 + O_2 = 2H_2O$. On the otherhand CO combines with O_2 to form CO_2 which turns lime water milky.

$$2CO + O_2 = 2CO_2 ; \qquad CO_2 + Ca(OH)_2 = CaCO_3\downarrow + H_2O$$

8. Oxygen and chlorine. [*Ans* : See page-296]
9. HCl(*g*) and HBr(*g*). [*Ans* : See page-328]
10. HCl and HI. [*Ans* : See page-328]
11. HBr and HI. [*Ans* : See page-328]
12. HF and HCl. [*Ans* : See page-328]
13. Chlorine and bromine. [*Ans* : Cl_2 combines with H_2 in presence of sunlight to form HCl. $H_2 + Cl_2 = 2HCl$. Bromine can not combine with H_2 in the sunlight but combines with H_2 in presence of a catalyst to form HBr. $H_2 + Br_2 \xrightarrow[\text{cat}]{} 2HBr$. A paper soaked in starch solution on being introduced into Cl_2, the colour of paper does not change but in bromine the colour is changed to yellow.]
14. White phosphorus and red phosphorus. [*Ans* : See page-198]
15. CO and N_2O. [*Ans* : CO combines with Cl_2 to form an additive compound carbonyl chloride. $CO + Cl_2 = COCl_2$, but N_2O does not react with Cl_2. CO has got reducing power. It reduces black hot cupric oxide into red metallic copper. N_2O has got oxidising power. It oxidises red metallic Cu to black CuO.

$$CuO + CO = Cu + CO_2\uparrow ; \qquad Cu + N_2O = CuO + N_2$$

16. H_2S and SO_2. [*Ans :* A paper soaked in $(CH_3COO)_2Pb$ when introduced into a jar containing H_2S, turns black due to the formation of PbS. $(CH_3COO)_2Pb + H_2S = PbS\downarrow + 2CH_3COOH$. SO_2 can not change the colour of the paper soaked in lead acetate. SO_2 can reduce the acidified solution of $KMnO_4$ turning the pink colour of the solution to a clear colourless solution. H_2S though can decolourise the pink colour of the acidified $KMnO_4$ solution, the colourless solution turns turbid due to the deposition of S.

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$
$$2KMnO_4 + 5H_2S + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5S + 8H_2O.$$

17. Phosphorus acid and phosphoric acid. [*Ans :* See page219]

18. SO_3 and SO_2. [*Ans :* See page 255]

19. Sodium nitrite and sodium nitrate. [*Ans :* See page 135]

20. Sodium sulphate and sodium sulphite. [*Ans :* To an aqueous solution of Na_2SO_4, $BaCl_2$ solution is added when a white precipitate is obtained which is does not dissolve in HNO_3. When $BaCl_2$ solution is added to Na_2SO_3 solution, a white precipitate is obtained but the produced ppt dissolves in HNO_3.

$$Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2NaCl\ ; \qquad Na_2SO_3 + BaCl_2 = BaSO_3\downarrow + 2NaCl$$
$$BaSO_3 + 2HNO_3 = Ba(NO_3)_2 + SO_2 + H_2O]$$

21. Sodium carbonate and sodium bicarbonate. [*Ans :* See page 218 Phy. Chem.]

22. KCl and KBr. [*Ans :* See page 330]

23. KBr and KI. [*Ans :* See page 330]

24. HI and HF. [*Ans :* See page 330]

25. Fluorine and Chlorine. [*Ans :* See page 308]

26. $NaHCO_3$ and $NaHSO_4$. [*Ans :* See page 436 Phy. Chem.]

27. Dilute HCl and dilute H_2SO_4. [*Ans :* See the tests of acids page 318, 267]

28. Ammonia and phosphine. [*Ans :* See page 207]

29. Chlorine and iodine. [*Ans :* See page 309]

30. Iodine and graphite. [*Ans :* See page 304]

31. Bromine and nitrogen dioxide. [*Ans :* See page 300]

32. N_2O and NO. [*Ans :* See page 120]

33. Borax and boric acid : The aqueous soln of borax is alkaline as it undergoes hydrolysis yielding NaOH and H_3BO_3. Thus aqueous soln. of borax gives reddish violet colour with phenolpthalin. $Na_2B_4O_7 + 7H_2O = 4H_3BO_3 + 2NaOH$. But as boric acid is very weak acid it cannot change the colour of methyl orange. When glycerol is added to the aqueous soln. of boric acid, it forms a stable complex with the release of H^+ ion and acts as strong acid. It changes the colour of methyl orange from yellow to red.

[G] How would you separate the following ingradients from a mixture—

1. Oxygen and ozone. [*Ans :* See page 74]

2. Oxygen and nitrous oxide. [*Ans :* The mixture is passed through cold water when N_2O is absorbed in it and O_2 passes out. The absorbed N_2O is liberated when the water is heated.]

3. Oxygen and hydrogen. [*Ans :* The mixture is cooled to −190°C when O_2 is condensed to liquid O_2 and H_2 passes out.]

4. CO and CO_2. [*Ans :* The mixture is passed through lime water when CO_2 is absorbed in it to form $CaCO_3$ and CO passes out. The $CaCO_3$ thus obtained is treated with dil HCl when CO_2 is liberated and collected.

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$
$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

5. N_2 and NH_3. [*Ans :* The mixture is passed through cold water when NH_3 is absorbed in it and N_2 passes out. The aqueous solution of NH_3 when heated NH_3 is liberated.

$$NH_3 + H_2O = NH_4OH \qquad NH_4OH \xrightarrow[\Delta]{} NH_3\uparrow + H_2O.]$$

6. Carbon powder and manganese di-oxide.

[*Ans.* The mixture is burnt in air when carbon combines with O_2 to form CO_2 but MnO_2 remains unchanged. The CO_2 is collected in a gas jar and a burning Mg ribbon is introduced in it when CO_2 is reduced by Mg to form carbon.]

$$C + O_2 = CO_2\ ; \qquad CO_2 + 2Mg = 2MgO + C\downarrow$$

7. HBr and Br_2.

[***Ans.*** The mixture is passed over red P when Br_2 reacts to form PBr_3 but HBr passes out without any reaction. The PBr_3 when treated with water HBr is produced. $2P + 3Br_2 = 2PBr_3$.

$$PBr_3 + 3H_2O = 3HBr + H_3PO_3.$$

The HBr thus obtained is treated with conc. H_2SO_4 when Br_2 is liberated.

$$2HBr + H_2SO_4 = 2H_2O + Br_2 + SO_2]$$

8. HCl and Cl_2.

[***Ans.*** The mixture is passed through cold water when HCl is absorbed in cold water and Cl_2 passes out and is collected. The HCl in water is neutralised by NaOH when NaCl is obtained. The solution of NaCl is dried completely to get solid NaCl. The NaCl thus produced on treatment with conc. H_2SO_4 yields HCl.

$$NaOH + HCl = NaCl + H_2O. \qquad NaCl + H_2SO_4 = NaHSO_4 + HCl \uparrow.]$$

9. SO_2 and CO_2.

[***Ans.*** The gas mixture is passed through conc. HNO_3 when SO_2 reacts to produce H_2SO_4. CO_2 and the produced NO_2 pass out. This gas mixture is passed through a freezing mixture when NO_2 is condensed to form a yellow liquid and CO_2 passes out. The H_2SO_4 thus formed is heated with Cu when SO_2 is obtained

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2\ ; \qquad Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O]$$

10. Hydrogen and CO_2.

[***Ans.*** The mixture is passed through KOH solution. When K_2CO_3 is obtained and H_2 passes out. The K_2CO_3 on treatment with dil. HCl yields CO_2.

$$2KOH + CO_2 = K_2CO_3 + H_2O\ ; \qquad K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O]$$

11. H_2S and SO_2.

[***Ans.*** The mixture is passed through $FeSO_4$ solution when H_2S reacts to form black ppt of FeS but SO_2 passes out. FeS is collected and treated with dil. H_2SO_4 when H_2S is liberated.

$$FeSO_4 + H_2S = FeS + H_2SO_4 \qquad FeS + H_2SO_4 = FeSO_4 + H_2S \uparrow]$$

12. N_2 and CO_2.

[***Ans.*** The mixture is passed through KOH when CO_2 reacts to form K_2CO_3 but N_2 passes out. K_2CO_3 thus obtained is treated with dil. HCl when CO_2 is evolved.

$$2KOH + CO_2 = K_2CO_3 + H_2O\ ; \qquad K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O]$$

13. P_2O_3 and P_2O_5.

[***Ans.*** See page 211]

14. White P and red P.

[***Ans.*** The mixture is added to CS_2 when white P dissolves in CS_2 leaving behind the undissolved red P. The red P is separated by filtration. The filtrate on being evaporated white P is obtained.]

15. NO and NO_2.

[***Ans.*** The gas mixture is passed through $FeSO_4$ solution. When NO reacts with $FeSO_4$ to form a complex and NO_2 passes out. The complex so formed on heating evolves NO.

$$FeSO_4 + 5H_2O + NO = [Fe\,(H_2O)_5\,NO]\,SO_4]$$

16. NO and N_2O. [***Ans.*** Same process as above]

17. CO and NO.

[***Ans.*** The mixture is passed through $FeSO_4$ solution when CO passes out but NO forms a complex which on being heated evolves NO.]

[H] Explain why : (Physical Chemistry)

1. The law of conservation of mass is not strictly true. [***Ans.*** See page 13].

2. The converse of the law of constant proportions is not always correct.

[***Ans.*** See page 15]

3. There are exceptions of the law of multiple proportions. [***Ans.*** See page 18].

4. The law of reciprocal proportions is nothing but a corollary of equivalent proportions. [***Ans.*** See page 20]

5. The physical and chemical scales of atomic weight are not the same.

[***Ans.*** See page 40]

6. The normal density of a gas depends on normal temperature and pressure but the vapour density of a gas does not depend on the normal temperature and pressure of the gas.

[***Ans.*** See page 54]

7. 'Molecular weight of NaCl is 58·5—this statement is wrong, the correct statement should be 'the formula weight of NaCl is 58·5.

[*Ans.* See page 49]

8. During the determination of equivalent weight of zinc by H-displacement method,

(i) few drops of $CuSO_4$ solution should be added before the reaction starts.

(ii) The weight of zinc taken in the experiment must not exceed 0·1 mg.

(iii) Nitric acid should not be used in this experiment.

[*Ans.* See page 149 ; (iii) Zn does not liberate H_2 from HNO_3]

9. The correct equivalent weight of magnesium by oxidation method, cannot be obtained by burning magnesium in air.

[*Ans.* During the combustion of Mg in air, a part of magnesium combines with O_2 of air to form MgO and the other part combines with N_2 of air to form Mg_3N_2. So correct equivalent weight can not be obtained.]

10. The atomic weight of an element is either equals to its equivalent or simple multiple of the equivalent weight. [*Ans.* See page 144]

11. The equivalent weight of an element depends on the reaction it undergoes. [*Ans :* See page 145]

12. In the determination of equivalent weight of zinc—(i) The process should not be carried out in woulfe's bottle. (ii) Addition of sufficient amount of $CuSO_4$ solution is not justifiable. [*Ans :* See page 149]

13. Atomic weight of an element is a simple multiple of its equivalent weight. [*Ans :* See page 144]

14. The equivalent weight of alkali metals can not be determined by hydrogen displacement method. [*Ans :* See page 148 and 152]

15. Equivalent weight of an element is not constant. [*Ans :* See page 145]

16. Diamond and sodium chloride forms crystals of same shape, but they are not isomorphous. [*Ans :* See page 160, Exceptions to law of isomorphism]

17. All alkalis are bases but all bases are not alkalis. [*Ans :* See page 186]

18. All acids contain hydrogen but all hydrogen containing compounds are not acids. [*Ans :* See page 181]

19. Anhydrous HCl does not turns blue litmus red. [*Ans :* See page-185]

20. Hypophosphorous acid contains of hydrogen atoms but its basicity is 1. [*Ans :* See page 183]

21. Dilute acids are more stronger than the concentrated acids. [*Ans :* See page 184]

22. Hydrogen chloride in its gaseous or liquid state does not exhibit acid property but it does in its aqueous solution. [*Ans :* See page 185]

23. NaOH is a base but ClOH is an acid. [*Ans :* See page 191]

24. Inspite of the absence of H atom in $AlCl_3$, it is a Lewise acid. [*Ans :* See page 191]

25. The addition of Na_2CO_3 solution on $FeCl_3$ or $AlCl_3$ solution, the respective carbonates are not precipitated. [*Ans. :* See page 432]

26. In many cases the metallic oxides are acidic. [*Ans :* See page 186 and 196]

27. The aqueous solution of $NaHCO_3$ is alkaline whereas the aqueous solution of $NaHSO_4$ is acidic. [*Ans :* See page 436]

28. Na_2HPO_4 is a normal salt. [*Ans :* See page 193]

29. H_3PO_3 is a dibasic acid. [*Ans :* See page 183]

30. Both H_2SO_4 and NaOH contain OH group, but the former is an acid while the latter is an alkali. [*Ans :* In NaOH, the OH^- is linked by an electrovalent bond to Na^+ which is highly electro positive and so OH^- cannot release H^+ ions. But in H_2SO_4, H atom is linked to oxygen atom by covalent bond. Now O atom is electro negative, so H atom can easily be released as H^+]

31. Na_2CO_3 though a normal salt, its aqueous solution exhibits alkaline property. [*Ans :* See page 433, hydrolysis of Na_2CO_3]

32. Though NH_3 is not a metallic oxide or hydroxide but it is considered as a base. [*Ans* : See page 185]

33. Phenolphthelein can not be used as an indicator in the tritration of Na_2CO_3 with strong acids. [*Ans* : See page 218]

34. ZnS is not precipitated when H_2S is passed through an acidified solution of $ZnSO_4$. [*Ans* : See page 446]

35. Inspite of the presence of 3 replaceable H atoms in phosphoric acid, it behaves as dibasic acid. [*Ans* : See page 217 inorganic]

36. $Mg(OH)_2$ is sparingly soluble in water, but it is easily soluble in NH_4Cl solution. [*Ans* : See page 446]

37. The solubility of glauber's salt at first increases with the rise of temperature but decreases afterwards. [*Ans* : See page 300]

38. Polar compounds are generally soluble in polar solvents but they are not soluble in non-polar solvents. [*Ans* : See page 293]

39. Na_2CO_3, $10H_2O$ is efflorescent but $MgCl_2$, $6H_2O$ is deliquescent when left exposed in air. [*Ans* : See page 312]

40. Water is a versatile solvent. [*Ans* : See page-53 inorganic]

41. Industrial chimneys emitting smokes have charged plates. [*Ans* : See page-325]

42. The solubility of sugar in a cup of water is not same in Calcutta and Darjeeling. [*Ans* : See page-298]

43. NH_4OH along with NH_4Cl are added during the precipitation of metals of Gr. IIIA as hydroxides. [*Ans* : See page-445]

44. The solubility of a substance decreases, if heat is evolved during its dissolution. [*Ans* : See page-298 and 410]

45. The properties of K^+ is completely different from these of K. [*Ans* : See page-339]

46. The conductivities of HCl and CH_3COOH are different. [*Ans* : See page-341]

47. During electrolysis, oxidation takes place at the anode and reduction at cathode. [*Ans* : See page-351]

48. Na is not liberated at the cathode during the electrolysis of an aqueous solution of NaCl. [*Ans* : See page-348(b)]

49. At high temperature, silica replaces more acidic P_2O_5 from $Ca_3(PO_4)_2$. [*Ans* : See page-194 inorganic]

50. Chemical equilibrium is a dynamic equilibrium. [*Ans* : See page-384]

51. Reversible reactions never go to completion. [*Ans* : See page-386]

52. Mercury is a liquid metal and good conductor of electricity but it is not an electrolyte. [*Hints* : Hg is not electrolyte because it does not conduct electricity by ions—it conducts with the help of free electrons.]

53. The position of equilibrium can be known from the value of equilibrium constant. [*Ans* : See page-393]

54. Almost all the chemical reactions are reversible. [*Ans* : See page-411]

55. Different results are obtained by heating $CaCO_3$ in open and closed vessels respectively. [*Ans* : See page-413(7)]

56. Aqueous solution of ammonium formate is weakly acidic. [*Ans* : See page-435]

57. Sodium nitrate obtained is nature is always found to be contaminated with sodium iodate. [*Ans* : $NaNO_3$ is isomorphens with $NaIO_3$]

58. If solid iodine is heated in a open test tube it sublimes, but if it is heated slowly in a sealed test tube, it melts to a liquid. [*Ans* : At a fixed temperature and pressure, the solid, liquid and gaseous state of iodine can coexist in equilibrium. This particular temperature is known as triple point temperature and the pressure is known as triple point pressure. The triple point temperature of iodine is 114°C and triple point pressure of I_2 is 90 mm. When iodine is slowly heated in an open test tube, the pressure of iodine vapour never exceeds 90 mm. due to the escape of I_2 vapour into the atmosphere. As a result I_2 is directly converted to vapour from its solid state. Now if I_2 is heated in a closed test tube, the pressure of its vapour exceeds 90 mm. and as a result solid I_2 is converted into liquid state.]

59. The bond energy of fluorine is less than that of chlorine. [***Hints :*** The atomic radius of F atom is much less than that of Cl atom and so the bond distance of F—F in F_2 molecule is much lesser than the bond distance Cl—Cl in Cl_2 molecule. As a result the other electrons of the two F atoms in F_2 molecule, which are not involved in forming the electron pair, exert a strong repulsive force on each other. So the bond F—F becomes weak.]

60. The aqueous solution of $AlCl_3$ is acidic. [***Ans :*** See page-331]

61. Nitrogen is inert in nature while phosphorus is very active.

[***Ans :*** See page-92 and 199 inorganic]

62. P can form PCl_3 and PCl_5 but nitrogen can form only NCl_3.

[***Ans :*** See page-221 inorganic]

[I] Explain why : (Inorganic Chemistry)

1. On the electrolysis of fused CaH_2, hydrogen is liberated at the anode. [*I.I.T. '73*]

[***Ans.*** Ca is a strong electropositive metal and consequently it has a greater tendency to give up electrons than that of hydrogen. So during the reaction between Ca and H_2 the Ca atom gives up the two electrons of its outermost orbit and is converted to Ca^{++} ion and these two electrons are taken by 2 hydrogen atoms and thus they are converted to H^- ions. In the fused state CaH_2 ionises as $CaH_2 \rightleftharpoons Ca^{++} + 2H^-$ On passing electricity through this fused CaH_2, H^- ion is liberated at the anode as H_2, by releasing its extra electrons.]

2. By the action of Zn on HCl, hydrogen is liberated more readily but, hydrogen evolves slowly when Zn is reacted with acetic acid.

[***Hints.*** HCl is a strong acid and so most of its molecules dissociates as H^+ and Cl^- ions. As CH_3COOH is a weak acid, lesser number of its molecules are dissociated as H^+ and CH_3COO^- and so concentration of H^+ is much greater in case of HCl than that of acetic acid.]

3. H_2 is evolved by the action of Zn on dil. H_2SO_4, but H_2 is not evolved by the action of Cu on dil. H_2SO_4. [***Ans.*** see page-23]. [*I.I.T. '74*]

4. A small amount of acid or alkali is added before the electrolysis of water.

[*I.I.T. '73*]

[***Hints.*** Pure water is a weak-electrolyte and so a bad conductor of electricity. Consequently to make water a good conductor, small amount of acid or alkali is added to it. See page 348 Phy. Chems.]

5. A solution of $FeCl_3$ acidified with HCl is uneffected when H_2 gas is bubbled through it but gets reduced when a piece of Zn is added to the same acidified solution.

[***Ans.*** see nasent hydrogen page-31]. [*I.I.T. '72*]

6. Water behaves both as an acid and an alkali.

[***Hints.*** See page 189 Phy. Chem.

In water the following equilibrium exists. $\underset{\text{weak acid}}{H_2O} + \underset{\text{weak base}}{H_2O} \rightleftharpoons \underset{\text{strong base}}{OH^-} + \underset{\text{strong acid}}{H_3O^+}$]

7. Hard water is softened before it is used in boilers. [***Ans.*** see page-48.]

8. Water extinguishes most fires but it can not extinguish petrol fire.

[***Ans.*** When water is applied on a fire it vaporises by taking latent heat from the burning materials. As a result the temperature of the burning materials is lowered down below their ignition point for which the fire extinguishes. But in case of petrol fire, petrol being lighter than water floats over water and gets much aerial O_2 and so fire spreads instead of being extinguished.]

9. Water is a liquid while H_2S is a gas at ordinary temperature. [***Ans.*** See page-237].

10. Water containing Ca^{2+} is Mg^{2+} ions, does not produce lathers with soap.

[***Ans.*** See page-39].

11. Anhydrous BaO_2 is not used in the preparation of H_2O_2 in the laboratory.

[***Ans.*** see page-61].

12. Phosphoric acid is preferred to H_2SO_4 in the preparation of H_2O_2 from BaO_2.

[***Ans.*** see page-60.]

13. The mixture of H_2O_2 and hydrazine with a Cu (II) catalyst is used as a rocket propellant.

[**Hints** : The reaction is highly exothermic and a large volume of gas is produced in this reaction.
$NH_2-NH_2+H_2O_2 \xrightarrow[\text{catalyst}]{Cu(II)} N_2(g)+4H_2O(g)$].

14. Discoloured old oil paintings may be restored to their original colours by the treatment with H_2O_2. [Ans. see page-65]. *[Roorkee Eng. '89]*

15. H_2O_2 is better oxidising agent them H_2O. [*Ans.* see page-65].

16. HCl or HNO_3 is not used in the preparation of H_2O_2 in the laboratory.
[*Ans.* see page-60]

17. H_2O_2 is not produced by the action of conc. H_2SO_4 on BaO_2. [*Ans.* see page-61]

18. Ozone is more stronger oxidising agent than oxygen. [*Ans.* see page-76]

19. Oxygen can reduce and hydrogen can oxidise. [*Ans.* See page-11 and 27].

20. At ordinary temperature O_2 is a gas but S is a solid. [*Ans.* See page-233].

21. Zn, Fe though electro-positive, do not evolve H_2 by their reaction with HNO_3.
[*Ans.* See page-126]

22. Soap does not form lathers in hard water, on prolonged rubbing small amount of lathers are formed. [*Ans.* See page-39]

23. Small amount of MnO_2 is added to $KClO_3$ during the preparation of O_2 in the laboratory. [*Ans.* See page-3]

24. Oxygen is a almost invariably exhibits an oxidation state of −2, but the other members of the group VI exhibit negative as well as positive oxidation state of +2, +4 and + 6. [*Ans.* See page-2] *[I.I.T. '88]*

25. Ozone layer acts as an umbrella for the earth against the harmful U.V. part of Sun's radiation.

[*Ans.* U.V. part of Sun's radiations decomposes oxygen molecules to form ozone in the ozonosphere. Ozone can absorb U.V. light. Thus ozone layer above earth's surface acts as a screen and prevents the U.V. radiation from reaching the earth's surface and thus saves us from the harmful effect of U.V. radiations.]

26. Water is thermally more stable than H_2S. [*Ans.* See page-2]

27. $KMnO_4$ should not be dissolved in Conc. H_2SO_4. [*Ans.* conc. H_2SO_4 forms an explosive covalent compound Mn_2O_7 with $KMnO_4$.

$$2KMnO_4+H_2SO_4=K_2SO_4+Mn_2O_7+H_2O.]$$

28. Ozone is an allotrope of oxygen. [*Ans.* See page-79]

29. Ozone is prepared by the silent electric discharge through dry and pure oxygen. [*Ans.* See page-75]

30. Mercury loses its mobility and lustre in ozone. [*Ans.* See page-76]

31. Distilled water is more pure than de-ionised water. [*Ans.* See page-45]

32. N_2 is diatomic but phosphorus is tetratomic. [*Ans.* See page-200]

33. The bottle containing liquor ammonia should be cooled before opening it.
[**Hints.** In liquor ammonia, NH_3 gas remains in water under great pressure. As soon as it is opened NH_3 gas comes out which may cause accident. As the solubility of gas increases with the decrease of temperature, to prevent the spurting of NH_3 the bottle should be cooled before opening]

34. Ammonia can produce complex compound.
[*Ans.* The N atom in NH_3 has lone pair of electrons which can combine with other atoms or cations by coordinate covalency to form complex. e.g. $[Cu(NH_3)_4]SO_4$

35. The boiling point of NH_3 is much higher than that of phosphine. *[I.I.T. '89]*
[*Ans.* See page-206]

36. Nitrogen is a gas while the other molecules of the group are solids.
[*Ans.* See page-200]

37. Nitrous oxide helps combustion. [*Ans.* See page-113]

38. HNO_3 acts only as an oxidising agent but HNO_2 acts both as an oxidising and reducing agents. [*Ans.* See page-126, 122]

39. HNO_3 turns yellow in sunlight. [*Ans.* See page-125]

40. NF_3 is stable but NCl_3 and NI_3 are explosives.

[***Hints.*** As the electronegativity of fluorine is much greater than that of nitrogen, and the atomic radius of F atom is small, the polarity of N—F bond is much strong. On the other hand the electronegativity of Cl or I is much less and the atomic radius of Cl or I atom is much bigger and as a result the bond distance N—Cl or N—I is greater and the polarity of N—Cl or N —I bond is much less than that of N—F bond.]

41. N_2 can not be prepared by heating NH_4NO_2 alone. [***Ans.*** See page-92]

42. N_2 is collected at room temperature by the displacement of cold water but N_2O is collected by that displacement of hot water. [***Ans.*** See page-112]

43. Burning Mg continues to burn in nitric oxide while burning S is extinguished.

[***Ans.*** Heat evolved during the burning of Mg is sufficient to decompose NO to N_2 and nascent oxygen and the nascent O helps the combustion of Mg. But the heat produced by the burning of S is much less and so NO molecule is not decomposed to produce nascent O]

44. During the production of NO from N_2 and O_2, the high temperature favours the production of NO. [***Ans.*** See page-138]

45. The water containing dissolved HCl or H_2SO_4, behaves as a hard water.

[***Ans.*** The water containing dissolved HCl or H_2SO_4 will behave as hard water. This is due to the fact that the HCl or H_2SO_4 of water will react with sodium stearate (soap) to produce NaCl or Na_2SO_4 and insoluble stearic acid)

$$\text{Na stearate} + HCl = NaCl + \text{stearic acid}$$

$$2\text{Na stearate} + H_2SO_4 = Na_2SO_4 + 2\ \text{stearic acid}$$

46. BaO_2 is called barium peroxide but MnO_2 is called manganese di-oxide.

[***Ans.*** see page-198 Phy chem.]

47. NO is a neutral oxide but it becomes acidic as soon as it comes in contact with air.

[***Ans.*** When NO comes contact with air, it is oxidised by the aerial O_2 to form NO_2 which is an acidic oxide. $2NO + O_2 = 2NO_2$].

48. NO is absorbed by $FeSO_4$ solution. [***Ans.*** See page-115]

49. NH_3 is more alkaline than PH_3. [***Ans.*** See page-206]

50. Iron does not react with con. HNO_3. [***Ans.*** See page-129]

51. A burning chip when introduced into a jar of NO, it extinguishes but a piece of phosphorus burns brilliantly in N_2O. [***Ans.*** See page-113 and 115].

52. Ammonia cannot be dried by P_2O_5 or $CaCl_2$ or conc. H_2SO_4. [***Ans.*** See page-100]

53. Ammonia liquefies more easily than methane.

[***Ans.*** N—H bond in NH_3 is more polar than the C—H bond in methane. Moreover NH_3 molecules exhibit hydrogen bondings among each other. So under a certain pressure when NH_3 molecules come closer to each other, they become associated by inter molecular H-bonding to a greater extend than that of CH_4].

54. Mercuric chloride when comes in contact with NH_3 becomes white but mercurous chloride in contact with NH_3 becomes black.

[***Ans.*** Mercuric chloride when comes in contact with NH_3 a white precipitate of amido mercuric salt is formed.

$HgCl_2 + 2NH_3 = Hg\,(NH_2)\,Cl \downarrow + NH_4Cl$. When mercurous chloride comes in contact with NH_3 amido mercuric chloride along with fine particles of metallic Hg are formed, as a result a black precipitate of black metallic Hg is observed.

$$Hg_2Cl_2 + 2NH_4OH = Hg\,(NH_2)\,Cl + Hg \downarrow + NH_4Cl + 2H_2O].$$

55. NH_3 can be prepared from HNO_3 and viceversa. [***Ans.*** See page-107]

56. HNO_3 can not be prepared by heating $NaNO_3$ with conc. HCl.

[***Ans.*** See page-124]

57. N_2 obtained from air is heavier than that obtained from $NaNO_2$.

[***Ans.*** See page-94]

58. Ammonium sulphate may be obtained without the help of H_2SO_4.

[***Ans.*** See page-107]

59. Conc. HNO_3 can be kept in an aluminium vessel but NaOH or KOH cannot be kept in an aluminium vessel. [***Ans.*** HNO_3 does not react with Al but NaOH or KOH reacts with Al with the formation of aluminate salt and H_2]

60. The density of red P is greater than that of white P. [***Ans.*** See page-199]

61. White P is more reactive and more volatile than red P. [***Ans.*** See page-199]

62. Phosphoric acid is tribasic but phosphorous acid is di-basic. [***Ans.*** See page-219]

63. Conc. H_2SO_4 or HNO_3 has got oxidising power. [***Ans.*** See page-126 and 265]

64. Red and white P are the allotropes of the same element. [***Ans.*** See page-200]

65. White P has reducing property. [***Ans.*** See page-201]

66. Phosphine prepared in the laboratory burns spontaneously. [***Ans.*** See page-203]

67. PH_4^+ is more stable than NH_4^+. [***Ans.*** NH_4^+ is more stable than PH_4^+. This is because of the fact that, P is more basic than N, consequently the hydride of P is less stable than that of N].

68. Na_3PO_4 is not easily prepared. [***Ans.*** See page 217].

69. Nitrogen is a gas but phosphorous is a solid. [***Ans.*** See page 200].

70. When white phosphorous comes in contact with hand it should be washed with $CaSO_4$ solution. [***Ans.*** See page 197].

71. The reducing power of phosphine is greater than that of ammonia. [***Ans.*** See page 206].

72. H_3PO_4 has reducing property but H_3PO_4 has no reducing property. [***Ans.*** See page 219 No. (5) point].

73. Phosphorus is not obtained in free state. [***Ans.*** See page 194].

74. White phosphorus is kept under water. [***Ans.*** See page 194].

75. During the preparation of phosphine, the air inside the flask is replaced by inert gas. [***Ans.*** See page 203].

76. The aqueous solution of Na_3PO_4 is alkaline. [***Ans.*** See page 217].

77. The m.p. of red P is higher than that of white P. [***Ans.*** See page 199].

78. H_3PO_4 behaves as a monobasic acid when titrated using methyl orange as indicator but as dibasic acid when phenolpthalein is used as indicator.

[***Ans.*** See page 217. The reaction of H_3PO_4 with NaOH takes place is three stages. When H_3PO_4 is titrated with NaOH using methyl orange as indicator, its colour changes from yellow to orange at the stage when NaH_2PO_4 is produced. When it is titrated against H_3PO_4 using phenolpthalein it turns pink when Na_2HPO_4 is produced].

79. Na_2HPO_3 is a normal salt. [***Ans.*** See page 215].

80. There is no existance of Na_2PO_3. [***Ans.*** See page 215].

81. PH_3 does not burns when it comes in contact with air, but phosphine produced in the laboratory by the action of white P an NaOH burns as soon as it comes in contact with air. [***Ans.*** See page 203].

82. The aqueous solution of borax is alkaline. [***Ans.*** See page 150].

83. The boiling point and melting point of boron is too much high. [***Ans.*** See page 147].

84. Boron does not form B^{3+} ion.

[***Ans.*** The atomic radii of boron atom is small and consequently its ionisation potential is high. As a result, electron transfer from boron atom is not possible to form B^{3+} ion].

85. Boric acid cannot be titrated with NaOH but it can be titrated against NaOH in presence of glycerol using phenolpthalein as indicator. [***Ans.*** See page 148].

86. Diamond cannot conduct eletricity but graphite is a good conductor of electricity. [***Ans.*** See page 160, 162].

87. Diamond is very hard whereas graphite is soft and lubricant. [***Ans.*** See page 160].

88. Diamond though convalent, its boiling point is very high. [***Ans.*** See page 160].

89. Carbon is used as an abrassive at the same time it can be used as a lubricant. [***Ans.*** See page 161, 162. See uses of diamond and graphite].

90. Coal gas is poisonous. [***Ans.*** See page 185].

91. CO_2 is a gas while SiO_2 is a solid. [*Ans.* See page 180].

92. Borax swells up on heating. [*Ans.* See page 150].

93. At ordinary temperature O_2 is a colourless gas but S is a pale yellow solid. [*Ans.* See page 233].

94. Aqueous solution of BCl_3 is acidic. [*Ans.* See page 146].

95. Diamond and graphite are the allotropes of the same element. [*Ans.* See page 167].

96. CO acts as a fuel as well as a reducing agent. [*Ans.* See page 170, 171].

97. Graphite is a lubricant. [*Ans.* See page 162].

98. CO possesses both oxidising and reducing properties but CO_2 has only oxidising property. [*Ans.* See page 177, 171].

99. Fire of Mg cannot be extinguished by CO_2. [*Ans.* See page 180].

100. Blue flame is found at the top of a coke oven.

[***Hints.*** Coke in presence of unsufficient supply of O_2 forms CO which burns with a blue flame
$2C + O_2 = 2CO$].

101. Aqueous soln. of H_2S becomes turbid when kept exposed in air. [*Ans.* See page 280].

102. Carbon monoxide cannot be dried by conc. H_2SO_4. [*J.E.E.* '85]

[*Ans.* See page 265].

103. Dil. H_2SO_4 cannot be concentrated beyond certain level by evaporation.

[*Ans.* Pure acid cannot be obtained from the dilute acid by evaporation as it forms a constant boiling mixture which boils at 338°C and which contains 98·3 percent of H_2SO_4].

104. SO_2 has got both oxidising and reducing power. [*Ans.* See page 249].

105. H_2S cannot be dried by conc. H_2SO_4 or $CaCl_2$ or CaO. [*Ans.* See page 236].

106. H_2S is more strong reducing agent than SO_2. [*Ans.* See page 239].

107. H_2S is a reducing agent—it can not oxidise. [*Ans.* See page 240].

108. H_2S cannot be prepared by the action of FeS on conc. H_2SO_4 or HNO_3. [*Ans.* See page 236].

109. H_2SO_4 is not used in the preparation of CO_2 from marble. [*Ans.* See page 175].

110. SO_2 can form additive compound but CO_2 cannot. [*Ans.* See page 249].

111. Sulphur when heated to 118°C melts to form a liquid but at 160°C—180°C it becomes viscous and loses its mobility. [*Ans.* See page 230].

112. Monoclinic and rhombic sulphur are the allotropes of the same element. [*Ans.* See page 233].

113. SO_3 is called the anhydride of H_2SO_4. [*Ans.* See page 253].

114. SO_2 or Cl_2 cannot bleach in absence of moisture. [Ans. See page 248].

115. H_2S burn with a blue flame. [*Ans.* See page 238].

116. SO_2 and CO_2 cannot be distinguished by using lime water. [*Ans.* See page 178].

117. Fluorine is very active metal. [*Ans.* See page 284].

Fluorine cannot be prepared by the electrolysis of HF. [*Ans.* See page 208].

118. HCl though a covalent compound, its aqueous solution can conduct electricity. [*Ans.* See page 317].

119. Hydrogen bromide or hydrogen iodide can not be prepared by the action of conc. H_2SO_4 on NaBr or NaI. [*Ans.* See page 319].

120. I_2 is sparingly soluble in water but it is very soluble in KI solution. [*Ans.* See page 303].

121. Cl_2 cannot bleach the printers ink. [*Ans.* Cl_2 does not react with carbon].

122. Fluorine cannot be oxidised. [*Ans.* See page 284].

123. I_2 can liberate Cl_2 from $KClO_3$. [*Ans.* See page 303].

124. Red colour of bromine water decolourises on exposure to sunlight but on prolong standing red colour of bromine reappears.

[***Ans.*** Br_2 reacts with H_2O in presence of sunlight form HBr and so bromine water becomes colourless, but on long standing the produced HBr is oxidised by aerial O_2 to form Br_2 and so the red colour reappears.

$H_2O + Br_2 = 2HBr + O\uparrow$; $2HBr + O_2 = H_2O + Br_2$].

125. F_2 is called super-halogen. [***Ans.*** See page 285].

126. H_2SO_4 cannot be prepared by heating Na_2SO_4 with conc. HCl. [*J.E.E. '82*] [***Ans.*** See page 265].

127. HI can not be dried by H_2SO_4 or CaO. [***Ans.*** See page 324].

128. HI is a reducing agent. [***Ans.*** See page 324].

129. H_2SO_4 cannot be prepared by passing SO_3 directly into water. [***Ans.*** See page 262].

130. HI is comparatively stable than other halogen acids. [***Ans.*** See page 325].

131. The m.p. of HF is higher than those of HCl or HBr. [***Ans.*** See page 311].

132. HF cannot be prepared in glass vessel. [***Ans.*** See page 311].

133. Pure NaCl is precipitated when hydrogen chloride is passed through an aqueous solution of brine. [***Ans.*** See page 444.(Phy. Chem.)].

134. HCl is stronger acid than HF. [***Ans.*** See page 315].

135. When blue litmus is added to hypochlorous acid at first it turns red but soon becomes colourless. [***Ans.*** See page 293].

136. HF, though monobasic, yields acid salts. [***Ans.*** See page 310].

137. The bleaching action of Cl_2 is parmanent but that of SO_2 is temporary. [***Ans.*** See page 293].

138. In the qualitative analysis, the gr II metals are precipitated in presence of HCl but not in presence of HNO_3.

[***Hints.*** As HNO_3 is an oxidising acid it liberates nasent oxygen which oxidises H_2S to form a precipitate of S. $2HNO_3 + 3H_2S = 2NO + 3S\downarrow + 4H_2O$].

139. HF is the weakest acid of all the halogen acids. [***Ans.*** See acidic property of HF].

140. Fluorine does not produce oxy-acids. [***Ans.*** See page 279].

141. The brown colour of the aqueous solution of a mixture of KI and I_2 becomes colourless on addition of a sulphite but becomes deeper on addition of a nitrite salt.

[***Ans.*** $KNO_2 + HCl = KCl + HNO_2$. The produced HNO_2 reduces KI to produce free I_2. The free I_2 gets mixed with KI to form KI_3 and so the brown colour becomes deeper.

$$2HNO_2 + 2KI = 2KOH + 2NO + I_2$$

$KI + I_2 = KI_3$. On the other case, the sulphite salt reacts with HCl to produce H_2SO_3 which reduces I_2 to form colourless HI and so the brown colour becomes colourless.

$Na_2SO_3 + 2HCl = H_2SO_3 + 2NaCl.$ $H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HF$].

[J] Identification of inorganic compounds with the help of chemical reactions.

1. A white crystalline solid *(A)* liberates a brown gas *(B)* on treatment with acid, or colourless alkaline gas *(C)* on treatment with NaOH and a colourless non-reactive gas *(D)* on heatings. If the heating of *(A)* is continued it disappears completely. Identify *A* to *D*. [*I.I.T. '82*]

Ans. The treatment of *(A)* with NaOH gives a alkaline gas NH_3 goes to prove that *(A)* is an ammonium salt. On heating *(A)* evolves a colourless non-reactive gas *(D)* which is nitrogen and it indicates that the ammonium salt *(A)* is nitrite. The different reactions are given below—

(i) $\underset{(A)}{NH_4NO_2} \xrightarrow[\Delta]{} \underset{(D)}{N_2} + 2H_2O$; (ii) $\underset{(A)}{NH_4NO_2} + NaOH = \underset{(C)}{NH_3} + NaNO_2 + H_2O$;

(iii) $NH_4NO_2 + HCl = NH_4Cl + HNO_2$

(iv) $2HNO_2 = H_2O + 2NO + O$; $2NO + O = \underset{(B)}{2NO_2}$ (brown)

2. An aqueous solution of a gas *(X)* gives the following reactions.

(i) It decolourises acidified $KMnO_4$ solution.

(ii) On boiling it with H_2O_2, cooling and then adding an aqueous solution of $BaCl_2$, a precipitate is obtained which is insoluble in dilute HCl.

(iii) On passing H_2S in the solution, a white turbidity is obtained. Identify *(X)* and give equations of reactions at steps (i), (ii) and (iii). *[Roorkee '90]*

Ans. The aqueous solution of the gas decolourises $KMnO_4$ solution. So the gas may be SO_2. On treatment with H_2O_2 shows that H_2SO_3 (aqueous Soln. of the gas) is oxidised to form H_2SO_4 which gives white ppt with $BaCl_2$. So the gas X = Sulphur dioxide (SO_2). The different reactions are given below :—

$$H_2O + SO_2 = \underset{\text{aqueous soln.}}{H_2SO_3}$$

(i) $2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(ii) $H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$; $H_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2HCl$

(iii) $H_2SO_3 + 2H_2S = 3H_2O + 3S \downarrow$.

3. An unknown mixture contains one or two of the following : $CaCO_3$, $BaCl_2$, $AgNO_3$, Na_2SO_4, $ZnSO_4$ and NaOH. The mixture is completely soluble in water and the solution gives pink colour with phenolpthalein. When dil. HCl is gradually added to this solution, a ppt is formed which dissolves on further addition of the acid. What is/are present in the mixture ? Give equations to explain the formation of the precipitate and its dissolution. *[I.I.T. '81]*

Ans. (i) As the mixture is soluble in water and the solution is alkaline, it contains NaOH.

(ii) Since the aqueous solution of the mixture gives a precipitate with HCl which dissolves on adding excess of HCl it indicates that the mixture contains $ZnSO_4$ also. So the mixture must contain NaOH and $ZnSO_4$. The involved reactions are given below—(i) $ZnSO_4 + 4NaOH = Na_2ZnO_2 + Na_2SO_4 + 2H_2O$. Here Na_2ZnO_2 and Na_2SO_4 both are soluble in water. (ii) On addition of HCl : $Na_2ZnO_2 + 2HCl = 2NaCl + \underset{\text{white ppt}}{Zn(OH)_2} \downarrow$.

$$Zn(OH)_2 + \underset{\text{excess}}{2HCl} = \underset{\substack{\text{soluble}\\\text{in water}}}{ZnCl_2} + 2H_2O$$

4. (i) An inorganic iodide *(A)* on heating with a solution of KOH gives a gas *(B)* and the solutions of the compound *(C)*. (ii) The gas *(B)* on ignition in air gives a compound *(D)* and water. (iii) Copper sulphate is finally reduced to the metal on passing *(B)* through its solution. (iv) A precipitate of compound *(E)* is formed on reaction of *(C)* with $CuSO_4$ solution. Identify *(A)* to *(E)* and give chemical equations for reactions at steps (i) to (iv). *[Roorkee Eng. '94]*

Ans. The inorganic iodide with KOH gives a gas *(B)* and a compound *(C)*. The gas *(B)* on ignition in air gives a compound *(D)* and water. So the compound *(B)* must contain H_2 and the iodide is phosphonium iodide.

$(A) = PH_4I$, $(B) = PH_3$, $(C) = KI$, $(D) = P_2O_5$, $(E) = Cu_2I_2$.

Reactions : (i) $\underset{(A)}{PH_4I} + KOH = \underset{(C)}{KI} + \underset{(B)}{PH_3} + H_2O$.

(ii) $\underset{(B)}{2PH_3} + 4O_2\,(\text{air}) \xrightarrow[\text{ignition}]{} \underset{(D)}{P_2O_5} + 3H_2O$

(iii) $\underset{(B)}{2PH_3} + 6CuSO_4 = Cu_3P_2, 3CuSO_4 + 3H_2SO_4$

$Cu_3P_2, 3CuSO_4 + 6H_2O = 6Cu \downarrow + 3H_2SO_4 + 2H_3PO_3$

(iv)
$$\begin{array}{rcl} 2CuSO_4 + 4KI & = & 2K_2SO_4 + 2CuI_2 \\ 2CuI_2 & = & 2CuI \downarrow + I_2 \\ \hline 2CuSO_4 + 4KI & = & 2K_2SO_4 + \underset{(E)}{2CuI} \downarrow + I_2 \end{array}$$

5. The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown pricipitate with an alkaline solution of K_2HgI_4. The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4, red vapours *(A)* are produced. The aqueous solution of the mixture gives a deep blue colouration

(B) with $K_3[Fe(CN)_6]$ solution. Identify the radicals in the given mixture and write balanced equations for the formation of *A* and *B*. *[I.I.T. '91]*

Ans. From the reactions given above we get the following inferences—

(i) The evolution of a gas (NH_3) on heating the mixture with NaOH, and the reddish brown precipitate on addition of alkaline solution of K_2HgI_4 indicates the presence NH_4^+ ion in the mixture.

(ii) A white precipitate ($BaSO_4$) is obtained when the solution of the mixture was treated with $BaCl_2$ solution which is sparingly soluble in conc. HCl. This goes to prove that SO_4^{2-} ions are present in the mixture.

(iii) The mixture on being heated with $K_2Cr_2O_7$ and conc. H_2SO_4 evolves red vapours (chromyl chloride). This indicates the presence Cl^- ions in the mixture.

(iv) The aqueous solution of the mixture when treated with $K_3[Fe(CN)_6$ goes to prove the presence of Fe^{2+} ions in the mixture.

Hence the mixture contains the following ions Fe^{2+}, NH_4^+, SO_4^{2-} and Cl^-.

The required chemical equations for the formation of *(A)* and *(B)* are—

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \xrightarrow[\Delta]{} K_2SO_4 + 2Na_2SO_4 + \underset{\text{chromyl chloride (red vapours) (A)}}{2CrO_2Cl_2} + 3H_2O$$

$$3Fe^{2+} + 2K_3[Fe(CN)_6] = \underset{\text{(Blue ppt) (B)}}{Fe_3[Fe(CN)_6]_2} + 6K^+$$

6. A black coloured compound *(A)* on reaction with dil. H_2SO_4 gives a gas *(B)* which on passing through a solution of acid *(C)* gives a white turbidity *(D)*. Gas *(B)* when passed through an acidified solution of a compound *(E)* gives a precipitate *(F)* soluble in HNO_3. After boiling this solution when an excess of NH_4OH is added, a blue coloured compound *(G)* is formed. To this solution on additions of acetic acid and aqueous solution of $K_4[Fe(CN)_6]$ a chocolate brown precipitate *(H)* is obtained. On addition of an aqueous solution of $BaCl_2$ to an aqueous solution *(E)* a white precipitate insoluble in HNO_3 is obtained. Identify from *(A)* to *(H)*.

[Roorkee Eng. '87]

Ans. The reactions can be expressed as follows—

$$\begin{tikzcd}
\text{Black compd } (A) \arrow[r, "\text{dil}", "H_2SO_4"'] & (B)\text{ gas} \arrow[r, "\text{acid } (C)"] \arrow[d, "\text{acidified solution } (E)"] & \text{White turbidity } (D) & \\
& \text{Precipitate } (F)\text{ Soluble in } HNO_3 \arrow[r, "HNO_3"] & \text{Solution} \arrow[r, "\text{boil}", "NH_4OH"'] & \text{blue compd } (G) \arrow[d, "\text{acetic acid} + K_4Fe(CN)_6"] \\
\text{Aqueous solution } (E) \arrow[r, "BaCl_2", "\text{soln.}"'] & \text{White ppt insoluble in } HNO_3 & & \text{chocolate ppt } (H)
\end{tikzcd}$$

From the above reactions we can get the following inferences —

(i) The aqueous solution *(E)* on treatment with $BaCl_2$ solution yields a white ppt which is insoluble in HNO_3. This indicates the presence of SO_4^{2-} ions in *(E)*.

(ii) The blue compound *(G)* on treatment with acetic acid and $K_4[Fe(CN)_6]$ yields a chocolate brown ppt *(H)*. This goes to prove that *(G)* must contain Cu^{2+} and so *(H)* must be cupric ferro cyanide $Cu_2[Fe(CN)_6]$.

(iii) As *(G)* is obtained from *(F)*, so compound *(F)* must contain Cu^{2+} ions. Again *(F)* is obtained by passing *(B)* gas through acidified solution *(E)*. So *(E)* also contains Cu^{2+} ion. The precipitate of Cu^{2+} ion is soluble in HNO_3, so *(F)* must be CuS and *(B)* is H_2S.

(iv) Aqueous solution *(E)* gives a white ppt insoluble in HNO_3 confirms the presence of SO_4^{2-} ions in *E*. So compound *(E)* must be $CuSO_4$.

(v) The gas *(B)* i.e. H_2S is obtained by the action of dil. H_2SO_4 on a black compound *(A)*. Hence *(A)* must be the sulphide of Cu or Fe or Pb or Hg etc.

Thus the formation of compounds *(A)* to *(H)* and their reactions may be expressed as—

$$\text{(i)}\ \underset{\text{(A)}}{FeS} + \underset{\text{dil}}{H_2SO_4} = FeS + \underset{\substack{\text{Hydrogen sulphide}\\ \text{(B)}}}{H_2S}$$

$$\text{(ii)}\ \underset{\text{(B)}}{H_2S} + \underset{\text{(C)}}{2HNO_3} = 2H_2O + 2NO_2 + \underset{\text{turbidity (D)}}{S\downarrow}$$

$$\text{(iii)}\ \underset{\text{(E)}}{CuSO_4} + H_2S = \underset{\substack{\text{copper sulphide}\\ \text{(F)}}}{CuS} + H_2SO_4$$

$$\text{(iv)}\ 3CuS + \underset{\text{(C)}}{8HNO_3} = \underset{\text{solution}}{3Cu(NO_3)_2} + 2NO + 3S + 4H_2O$$

$$\text{(v)}\ 2Cu(NO_3)_2 + 2NH_4OH = Cu(NO_3)_2, Cu(OH)_2 + 2NH_4NO_3$$

$$Cu(NO_3)_2, Cu(OH)_2 + 2NH_4NO_3 + 6NH_2OH = \underset{\substack{\text{cupro ammonium salt deep}\\ \text{blue compound (G)}}}{2[Cu(NH_3)_4](NO_3)_2} + 8H_2O$$

$$\text{(vi)}\ [Cu(NH_3)_4](NO_3)_2 + 4CH_3COOH = Cu(NO_3)_2 + 4CH_3COONH_4$$

$$\text{(vii)}\ 2Cu(NO_3)_2 + K_4[Fe(CN)_6] = \underset{\text{chocolate ppt (H)}}{Cu_2[Fe(CN)_6]\downarrow} + 4KNO_3$$

$$\text{(viii)}\ \underset{\text{(E)}}{CuSO_4} + BaCl_2 = \underset{\substack{\text{insoluble in}\\ HNO_3}}{BaSO_4\downarrow} + CuCl_2$$

$A = FeS$; $B = H_2S$; $C = HNO_3$; $D = S$; $E = CuSO_4$; $F = CuS$; $G = [Cu(NH_3)_4](NO_3)_2$; $H = Cu_2[Fe(CN)_6]$

7. Compound *(A)* is a light green crystallion solid. It gives the following tests—

(a) It dissolves in dil. H_2SO_4 and no gas is evolved.

(b) One drop of $KMnO_4$ is added to the above solution. The pink colour disappears.

(c) Compound *(A)* is heated strongly. Gases *(B)* and *(C)* having pungent smell are evolved. A brown residue *(D)* is left behind.

(d) The gas mixture of *(B)* and *(C)* is passed through a dichromate solution when the solution turns green.

(e) The green solution from step (d) gives a white precipitate *(E)* with barium nitrate solution.

(f) Residue *(D)* from step (c) is heated on a charcoal block in a reducing flame. It gives a black magnetic mass. Name the compounds *(A)*, *(B)*, *(C)*, *(D)* and *(E)*.

[*I.I.T. '80*]

Ans. (i) Since the brown residue on heating on a charcoal block gives a magnetic mass, so the residue is iron. The compound *(D)* and hence compound *(A)* are also iron compounds. This is further confirmed by the light green colour of *(A)*.

(ii) The compound *(A)* being treated with acidified $KMnO_4$ solution, discharges the violet colour of $KMnO_4$ by reduction, so the compound *(A)* must be ferrous sulphate.

(iii) The compound *(A)* on being strongly heated give gases *(B)* and *(C)* having pungent smell and which turns $K_2Cr_2O_7$ soln. green. The green compound *(A)* when treated with $Ba(NO_3)_2$ a white ppt *(E)* is obtained. This goes to prove that the *(A)* compound must be sulphate and *(B)* and *(C)* gases are SO_2 and SO_3.

Thus, *A* = Ferrous sulphate $FeSO_4$, *B* = Sulphur di-oxide SO_2, *C* = Sulphur tri-oxide SO_3, *D* = Ferric oxide Fe_2O_3, *E* = Barium sulphate, $BaSO_4$.

Reactions : (i) $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$.

(ii) $10\,FeSO_4 + 8\,H_2SO_4 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$.

(iii) $FeSO_4 + Ba(NO_3)_2 = BaSO_4\downarrow + Fe(NO_3)_2$.

(iv) $Fe_2O_3 + 3C = 2Fe + 3CO$.

8. An aqueous solution of a gas *(X)* shows the following reactions.

(i) It turns red litmus blue.

(ii) When added in excess to $CuSO_4$ solution deep blue colour is obtained.

(iii) On addition to ferric chloride solution a brown precipitate soluble in dilute HNO_3 is obtained.

Identify *(X)* and give equations for the reactions at steps (ii) and (iii).

[*Roorkee Eng. '91*]

Ans. (i) The aqueous solution of the gas turns red litmus blue—this indicates that the gas is of basic nature.

(ii) It produces—compound of deep blue solution with $CuSO_4$ solution. This indicates that the compound of deep blue solution is cupro ammonium sulphate and the gas *(X)* is NH_3.

(iii) The gas when passed through $FeCl_3$ solution yields a brown ppt which indicates that the brown ppt is $Fe(OH)_3$ which is produced by the action of NH_4OH on $FeCl_3$.

Hence *(X)* is ammonia gas NH_3.

Reactions :

$$CuSO_4 + 4\underset{(x)}{NH_3(aq)} = \underset{\substack{\text{cupro ammonium}\\\text{sulphate}}}{[Cu(NH_3)_4]SO_4}$$

$$FeCl_3 + 3NH_4OH = \underset{\text{brown ppt}}{Fe(OH)_3\downarrow} + 3NH_4Cl$$

$$Fe(OH)_3 + 3HNO_3 = Fe(NO_3)_3 + 3H_2O.$$

9. A white powder (*A*) on being heated gives off a colourless gas (*B*) which turns lime water milky and the residue (*C*) which is yellow when hot but white when cold. (*C*) dissolves in dil HCl and the resulting solution gives a white precipitate on addition of $K_4[Fe(CN)_6]$ solution. (*A*) dissolves in dil HCl with the evolution of a gas which is identical with (*B*) in all respects. The solution of (*A*) as obtained above gives a white precipitate (*D*) on addition of excess of NH_4OH and passing H_2S. Another portion of the solution gives initially a white precipitate (*E*) on addition of NaOH solution which dissolves on further addition of the base. Identify (*A*) to (*E*).

[*I.I.T. '79*]

Ans : Gas (*B*) turns lime water milky, so the gas may be CO_2 or SO_2 and consequently the compound (*A*) may be carbonate or sulphite. Since the residue (*C*) which is oxide, becomes yellow when hot and white when cold indicates that it must be ZnO.

Hence A = Zinc carbonate $ZnCO_3$, B = Carbon dioxide CO_2, C = Zinc oxide ZnO, D = ZnS and E = $Zn(OH)_2$.

Reactions :

$$\underset{(A)}{ZnCO_3} \xrightarrow[\Delta]{} \underset{(C)}{ZnO} + \underset{(B)}{CO_2}\,; \qquad \underset{(C)}{ZnO} + 2HCl = ZnCl_2 + H_2O.$$

$$2ZnCl_2 + K_4[Fe(CN)_6] = \underset{\text{white ppt}}{Zn_2[Fe(CN)_6]\downarrow} + 4KCl.$$

$$\underset{(A)}{ZnCO_3} + 2HCl = ZnCl_2 + \underset{(B)}{CO_2} + H_2O$$

$$ZnCl_2\,(\text{alkaline}) + H_2S = \underset{\text{white ppt (D)}}{ZnS} + 2HCl$$

$$ZnCl_2 + 2NaOH = \underset{\text{white ppt (E)}}{Zn(OH)_2} + 2NaCl$$

$$Zn(OH)_2 + 2NaOH = \underset{\text{soluble}}{Na_2ZnO_2} + 2H_2O$$

10. When a non combustible gas is passed over hot magnesium and the product is reacted with water, a new gas is produced. When this new gas is passed over hot cupric oxide the original gas is obtained. What is the name of the gas ? Give equations of the reactions involved.

[*J.E.E. '90*]

Ans : The gas is nitrogen. This gas being passed over hot Mg produces magnesium nitride Mg_3N_2, which reacts with water to produce ammonia. Ammonia on being passed over hot cupric oxide is oxidised to give N_2.

Reactions : $3Mg + N_2 = Mg_3N$.

$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$; $\qquad 2NH_3 + 3CuO = 3Cu + N_2 + 3H_2O$

11. A compound (*A*) gives off a pungent smelling gas on boiling with NaOH solution and a red litmus paper turns blue on holding over the test tube. A solution of (*A*) liberates a colourless gas (*B*) on gentle heating. A solution of (*A*) gives a transcient blue solution on the addition of dil H_2SO_4, then it evolves a brown gas (*C*). Identify (*A*), (*B*) and (*C*), give reasons.

Ans : Compound (*A*) on heating with NaOH evolves a pungent smelling gas which is basic in nature as shown by litmus paper, so the gas is NH_3.

Now NH_3 comes from ammonium salt. Again the ammonium salt gives a colourless gas on heating gently. So the evolved gas is N_2 and the salt is ammonium nitrite.

Ammonium nitrite with dil H_2SO_4, at first produces nitrous acid and ammonium sulphate solution. This is transcient blue in colour. HNO_2 on heating evolves brown gas NO_2.

Equation of reactions :

$$\underset{(A)}{NH_4NO_2} + NaOH = NH_3 + NaNO_2 + H_2O$$

$$NH_4NO_2 \xrightarrow[\Delta]{} \underset{(B)}{N_2} + 2H_2O$$

$$2NH_4NO_2 + H_2SO_4 = \underset{\text{transcient blue soln.}}{2HNO_2 + (NH_4)_2SO_4}$$

$$2HNO_2 = 2NO + H_2O + O \;; \qquad 2NO + O = \underset{\text{brown gas (C)}}{2NO_2}$$

12. A gas evolved by treating sodium sulphide with water is passed through ammoniacal zinc chloride solution when a precipitate is obtained. What is the colour and composition of the precipitate ? What happens when the precipitate is treated with HCl followed by NaOH solution ? [*J.E.E.* '*91*]

Ans : (i) On addition of water to Na_2S, hydrogen sulphide is evolved. $Na_2S + 2H_2O = 2NaOH + H_2S \uparrow$.

(ii) When the evolved H_2S is passed through ammoniacal $ZnCl_2$ a white precipitate of ZnS is obtained. $ZnCl_2 + H_2S = ZnS \downarrow\ 2HCl$.

(iii) ZnS (white ppt) on treatment with HCl, Zinc chloride is produced. $ZnS + 2HCl = ZnCl_2 + H_2S$.

(iv) $ZnCl_2$ when treated with NaOH at first a white precipitate of zinc hydroxide is obtained. On addition of excess of NaOH, water soluble sodium zincate is formed and as a result the ppt of $Zn(OH)_2$ dissolves.

$$ZnCl_2 + 2NaOH = Zn(OH)_2 + 2NaCl$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

13. A colourless solid (*A*) on being heated gives another solid (*B*) and O_2. (*B*) with dil HCl evolves a brown gas. (*B*) on being heated with ammonium chloride yields a colourless gas and a residue (*C*). (*A*) when heated with ammonium chloride yields a colourless gas and a residue which is similar to (*C*) in all respects. This residue imparts a golden yellow flame in the bunsen burner. Identify (*A*), (*B*) and (*C*). [*J.E.E.* '*86*]

Ans : (i) (*A*) When heated yields a solid (*B*) with the evolution of O_2. Again (*B*) imparts golden yellow flame in the bunsen burner. Hence the solid (*A*) must be sodium nitrate which on heating gives sodium nitrite and O_2. $\underset{(A)}{2NaNO_3} = \underset{(B)}{2NaNO_2} + O_2$

(ii) The residue $NaNO_2$ when heated with NH_4Cl evolves nitrogen leaving a residue NaCl.

$$NH_4Cl + \underset{(B)}{NaNO_2} = NH_4NO_2 + \underset{(C)}{NaCl} \xrightarrow[\Delta]{} \underset{\text{colourless gas}}{N_2} + 2H_2O + NaCl$$

(iii) The residue $NaNO_2$ (*B*) on treatment with HCl evolves NO_2 which is brown.

$$2NaNO_2 + 2HCl = 2NaCl + NO + NO_2 + H_2O, \quad NO + O = \underset{\text{brown gas}}{NO_2}$$

(iv) $NaNO_3$ (*A*) when heated with NH_4Cl gives NaCl (*C*) and nitrous oxide.

$$NaNO_3 + NH_4Cl = \underset{(C)}{NaCl} + NH_4NO_3 \xrightarrow[\Delta]{} \underset{\underset{(C)}{\text{residue}}}{NaCl} + N_2O + 2H_2O.$$

14. An orange coloured solid (*A*) on heating gave a green residue (*B*), a colourless gas (*C*) and water vapour. The dry gas (*C*) on passing over heated Mg gave a white solid (*D*). (*D*) on reaction with water gave a gas (*E*) which formed dense white fumes with HCl. Identify (*A*) to (*E*) and give the reactions involved. [*I.I.T.* '*93*]

Ans : (i) Since (*E*) gives dense white fumes with HCl, it is ammonia. (ii) This ammonia is obtained by the reaction of the white solid which is obtained by passing the colourless gas (*C*) with Mg. Hence the white solid (*D*) is magnesium nitride and the gas (*C*) is nitrogen. (iii) As the yellow solid (*A*) gives N_2 on heating so the yellow solid is ammonium dichromate. (iv) Ammonium dichromate on heating evolves N_2 leaving a green residue of chromic oxide. So (*B*) is chromic oxide.

Thus, A = Ammonium dichromate, B = Chromic oxide, C = Nitrogen,
D = Magnesium nitride, E = Ammonia.

Reactions :

$$\underset{(A)}{(NH_4)_2Cr_2O_7} \xrightarrow[\Delta]{} \underset{(B)}{Cr_2O_3} + \underset{(C)}{N_2} + 4H_2O$$

$$3Mg + \underset{(C)}{N_2} = \underset{(D)}{Mg_3N_2}\ ; \qquad \underset{(D)}{Mg_3N_2} + 6H_2O = 3Mg(OH)_2 + \underset{(E)}{2NH_3}$$

$$NH_3 + HCl = \underset{\text{dense white fumes}}{NH_4Cl}$$

15. A certain metal (*A*) is boiled with dilute HNO_3 to give a salt (*B*) and an oxide of N_2 (*C*). An aqueous solution of (*B*) with brine gives a precipitate (*D*) which is soluble in excess of NH_4OH. On adding aqueous solution of (*B*) to hypo solution, a white precipitate (*E*) is obtained. (*E*) on standing turns to a black compound (*F*). Identify (*A*) to (*F*). [*Roorkee Eng. '90*]

Ans : An aqueous solution of (*B*) with brine (NaCl) gives a precipitate (*D*) which is soluble in excess of NH_4OH. This information indicates that (*D*) is silver chloride (AgCl). Consequently the metal (*A*) is silver and the compound (*B*) must be silver nitrate $AgNO_3$. This inference is supported by the fact that silver nitrate (*B*) being added to hypo solution ($Na_2S_2O_3$) gives a white precipitated of silver thiosulphate $Ag_2S_2O_3$ which turns black due to the formation of silver sulphide (*F*). Thus, A = silver, B = silver nitrate ($AgNO_3$), C = nitric oxide NO, D = silver chloride, AgCl, E = silver thiosulphate, $Ag_2S_2O_3$, (F) = silver sulphide, Ag_2S.

Reactions :

$$\text{(i)}\ \underset{(A)}{3Ag} + 4HNO_3 = \underset{(B)}{3AgNO_3} + \underset{(C)}{NO} + 2H_2O$$

$$\text{(ii)}\ \underset{(B)}{AgNO_3} + NaCl = \underset{(D)}{AgCl\downarrow} + NaNO_3$$

$$\text{(iii)}\ AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$$

$$\text{(iv)}\ 2AgNO_3 + Na_2S_2O_3 = \underset{(E)}{Ag_2S_2O_3\downarrow} + 2NaNO_3$$

$$\text{(v)}\ \underset{(E)}{Ag_2S_2O_3} + H_2O = \underset{(F)}{Ag_2S\downarrow} + H_2SO_4$$

16. The acidic solution of Fe^{++} ion forms brown complex in presence of NO_3^- by the following two steps. Complete and balance the equations.

$$[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \longrightarrow \text{——} + [Fe(H_2O)_6]^{3+} + H_2O$$

$$[Fe(H_2O)_6]^{2+} + \text{——} \longrightarrow \text{——} + H_2O$$

[***Ans.*** $3[Fe(H_2O)_6]^{2+} + NO_3^- + 4H^+ = NO + 3[Fe(H_2O)_6]^{3+} + 2H_2O$
$[Fe(H_2O)_6]^{2+} + NO = [Fe(H_2O)_5NO]^{2+} + H_2O$.]

17. A light bluish green crystaline compound responds to the following tests —

(i) its aqueous solution gives a brown precipited with alkaline $K_2[HgI_4]$ solution.
(ii) its aqueous solution gives a blue colour with $K_3[Fe(CN)_6]$ solution.
(iii) its solution in HCl gives white precipitate with $BaCl_2$ solution.

Identify the ions present and suggest the formula of the compound. [*I.I.T. '92*]

Ans. (i) As the aqueous solution of the compound gives brown precipited or colouration with $K_2[HgI_4]$ solution, the compound must contains NH_4^+ radical.

(ii) Since its aqueous solution gives blue colour with $K_3[Fe(CN)_6]$, it must contain Fe^{2+} ions.

(iii) Its acidified solution with HCl gives white precipited with $BaCl_2$, so it must contain SO_4^{2+} ions. The compound is bluish green and crystalline which contains NH_4^+, Fe^{2+} and SO_4^{2+} radicals. Hence the salt is Mohr's salt of molecular formula $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$.

18. A green amorphous substance (*A*) on being heated a colourless gas (*B*) is liberated leaving a black residue (*C*). The gas (*B*) turns lime water milky. The residue (*C*) is dissolved in dil. HCl and the solution thus obtained on being treated with $K_4[Fe(CN)_6]$ yields a chocolate brown ppt. When (*A*) is dissolved in HCl, a gas is evolved which is identical with (*B*) in all respects, when H_2S gas is passed through the acidified solution of (*A*) a black ppt. (*D*) is obtained. To the other part of this solution when NaOH is added a ppt. (*E*) is obtained which remains unchanged inspite of addition of excess of alkali. Identify the compounds (*A*) to (*E*).

[**Ans.** The colourless gas (*B*) turns lime water milky, so the gas may be CO_2 or SO_2 and the compound (*A*) may be carbonate or sulphite. Since the residue (*C*) on treatment with HCl and $K_4[Fe(CN)_6]$ yields a chocolate brown ppt, which goes to prove that (*A*) is a compound of copper—either $CuCO_3$ or $CuSO_3$. Since $CuSO_3$ is unstable so (*A*) must be $CuCO_3$ and (*B*) is CO_2 and the black residue is CuO. $CuCO_3$ on treatment with HCl gives CO_2 (*B*) and a solution of $CuCl_2$. To this solution when H_2S is passed a black ppt of CuS is obtained which is (*D*). To other part of the solution of (*A*) when NaOH is added a ppt of $Cu(OH)_2$ is obtained (*E*). Hence : (*A*) = $CuCO_3$, (*B*) = CO_2, (*C*) = CuO, (*D*) = CuS, (*E*) = $Cu(OH)_2$

Reactions :

$$\underset{(A)}{CuCO_3} = \underset{(C)}{CuO} + \underset{(B)}{CO_2}, \qquad CuO + 2HCl = CuCl_2 + H_2O$$

$$2CuCl_2 + K_4[Fe(CN)_6] = \underset{\text{Chocolate brown ppt.}}{Cu_2[Fe(CN)_6]} + 4KCl,$$

$$CuCO_3 + 2HCl = CuCl_2 + \underset{(B)}{CO_2} + H_2O, \qquad CuCl_2 + H_2S = \underset{(D)}{CuS} + 2HCl$$

$$CuCl_2 + 2NaOH = \underset{(E)}{Cu(OH)_2} + 2NaCl$$

[K] Some important short answer type questions with their answers—

1. Mention the name of indicator used and the change of colour at the end point in case of the following titrations—

(a) NH_4OH against H_2SO_4, (b) CH_3COOH against NaOH.

[**Ans.** (a) indicator—methyl orange, change of colour—yellow to orange. (b) indicator—phenolpthalein, change of colour—pink to colourless.]

2. Identify the following—

(a) A compound which on heating evolves a gas having the smell of rotten fish.

[**Ans.** phosphorus acid. $4H_3PO_3 = 3H_3PO_4 + PH_3$ Phosphine has a smell of rotten fish.]

(b) A white solid which on being heated, evolves a brown gas leaving a residue, the colour of which is brown when hot and yellow while cold.

[**Ans.** lead nitrate $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$ PbO is brown while hot and yellow while cold]

(c) An aqueous solution of a calcium salt which on being heated, evolves a colourless and odourless gas with the formation of white precipitate.

[**Ans.** Calcium bicarbonate, the white precipitate is of calcium carbonate.

$$Ca(HCO_3)_2 = CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$

(d) A salt which being heated with solid $K_2Cr_2O_7$ and conc. H_2SO_4 evolves a red vapour.

[**Ans.** Chloride salt, e.g. KCl, the red gas is chromyl chloride.

$$4KCl + K_2Cr_2O_7 + 3H_2SO_4 = \underset{\text{chromyl chloride}}{2CrO_2Cl_2} + 3K_2SO_4 + 3H_2O$$

(e) An element having different equivalent weights.

[**Ans.** Copper has different equivalent wt.—Cu (I) 63·5 Cu (II) 31·75

(f) A normal salt having hydrogen atom in it. [**Ans.** Disodium hydrogen phosphite Na_2HPO_3]

(g) A solid acidic oxide containing metal. [**Ans.** Manganese heptoxide Mn_2O_7]

(h) Anhydrides of NaOH, HNO_3 and H_3PO_4. [**Ans.** Na_2O, N_2O_5, P_2O_5]

(i) A reversible reaction in which $k_p \neq k_c$ *and a reversible reaction in which* $k_p = k_c$.

[**Ans.** $N_2 + 3H_2 \rightleftharpoons 2NH_3$ here $k_p \neq k_c$

$N_2 + O_2 \rightleftharpoons 2NO$ here $k_p = k_c$]

(j) A element which can not be oxidised. [**Ans.** fluorine F_2]

(k) A non metal which does not form any oxy acid. [**Ans.** fluorine F_2]

(l) Three compounds which exhibits hydrogen bond. [**Ans.** H_2O, HF, NH_3]

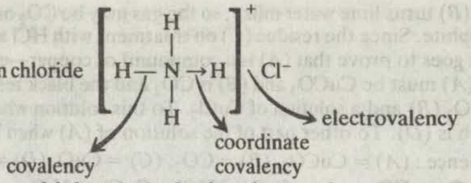
(m) A mono basic acid which can form acid salt.

[**Ans.** Hydrofluoric acid HF. acid salt is KHF_2]

(n) A Lewis acid containing metal. [**Ans.** $AlCl_3$]

(o) A compound having three types of valencies.

[*Ans.* Ammonium chloride



(p) 3 metallic ions which cause the hardness of water. [*Ans.* Ca^{2+}, Mg^{2+}, Fe^{2+}]

(q) Two reactions in which water acts as catalyst.

[*Ans.* $H_2 + Cl_2 \xrightarrow{H_2O} 2HCl$, $2Na + Cl_2 \xrightarrow{H_2O} 2NaCl$]

(r) A compound in which the oxidation number of oxygen is +2.
[*Ans.* Oxygen fluoride (OF_2)]

(s) An acid which dissolves gold and platinum. [*Ans.* Aqua regia ($3HCl + HNO_3$)]

(t) 2 metals which liberate H_2 from HNO_3. [*Ans.* Magnesium and manganese]

(u) A gas which loses the mobility of Hg. [*Ans.* ozone]

(v) A gas which is isoelectronic with CO. [*Ans.* N_2]

(w) A non metal dissolves in NaOH and gives a gas having smell of rotten fish.
[*Ans.* White P]

(x) A salt which swells up an heating. [*Ans.* Borax. $Na_2B_4O_7$, $10H_2O$]

3. Write down the formula and uses of the following—

(i) **Common alum**—[*Ans.* K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$. Used for the purification of water, in tanning leather, as a styptic to arrest bleeding].

(ii) **Plaster of Paris**—[*Ans.* $2CaSO_4$, (H_2O). Used in making moulds for casting. It is also used for making crayons.

(iii) **Washing soda**—[*Ans.* Na_2CO_3, $10H_2O$. Used for washing clothes and for making soaps]

(iv) **Bleaching powder**—[*Ans.* $Ca(OCl)Cl$. Used in bleaching and as a disinfactant]

(v) **Rust**—[*Ans.* A hydrated ferric oxide Fe_2O_3, $3H_2O$]

(vi) **Baking powder**—[*Ans.* ($NaHCO_3$ + tartaric acid). Used in the preparation of soft drinks and fruit salts as an antacid and in fire extinguisher]

(vii) **Green vitriol**—[*Ans.* $FeSO_4$, $7H_2O$. Used in the preparation of ink and rouge and as a mordant]

(viii) **Hypo**—[*Ans.* Sodium thiosulphate $Na_2S_2O_3$, $5H_2O$. Used in photography and in the extraction of Au and Ag]

(ix) **Laughing gas**—[*Ans.* Nitrous oxide N_2O. Used as an anaesthetic during surgery]

(x) **Alumina**—[*Ans.* Al_2O_3. Used in the extraction of Aluminium]

(xi) **Zinc white**—[*Ans.* ZnO. Used in the preparation of white paint]

(xii) **Blue vitriol**—[*Ans.* $CuSO_4$, $5H_2O$. Used for the identification of water, in making Daniels cell and in electroplating]

(xiii) **Oil of vitriol**—[*Ans.* H_2SO_4. Used in the preparation of fertilisers, storage battary and as dehydrating agent]

(xiv) **Aqua fortis**—[*Ans.* Nitric acid HNO_3, used for producing picric acid, nitro glycerine, TNT, artificial silk]

(xv) **Muriatic acid**—[*Ans.* Hydrochloric acid. Used in the preparation of Cl_2, in galvanisation]

(xvi) **Gypsum**—[*Ans.* $CaSO_4$, $2H_2O$. Used in the preparation of plaster of paris, ammonium sulphate]

(xvii) **Bordeaux mixture**—[*Ans.* ($CuSO_4$ solution + lime). Used to kill moulds and destroy fungi on wines]

(xviii) **Lithophone**—[*Ans.* ($ZnS + BaSO_4$). Used as white paint]

(xix) **Carbogen**—[*Ans.* (A mixture of O_2 and 10% CO_2). Used in the artificial respiration]

(xx) **Nitrolim**—[*Ans.* A mixture of calcium cyanamide and carbon ($CaCN_2$ + C). Used as fertiliser]

(xxi) **Fremy's Salt**—[*Ans.* See page 310]

(xxii) **Glaubers salt**—[*Ans.* Na_2SO_4, $10H_2O$. Used in the preparation of paper and glass]

(xxiii) **Fluosper**—[*Ans.* CaF_2. Used in the extraction of Al and in the preparation of HF]

(xxiv) **Soda lime**—[*Ans.* ($NaOH + Ca(OH)_2$). Used in the preparation of hydro carbon and as an absorbant of CO_2.]

(xxv) **Horn silver**—[*Ans.* AgCl. Used in the preparation of Ag]

(xxvi) **Lunar caustic**—[*Ans.* $AgNO_3$. Used as a reagent]

(xxvii) **Baryta**—[*Ans.* $BaSO_4$. Helps in getting X-ray pictures of stomach—also used as white pigment]

(xxviii) **Borax**—[*Ans.* $Na_2B_4O_7$, $10H_2O$. Used in the preparation of boro silicate glass and as a flux]

(xxix) **Epsom salt**—[*Ans.* $MgSO_4$, $7H_2O$. Used as medicine and in tanning]

(xxx) **Pearl ash**—[*Ans.* K_2CO_3. Used in the preparation of soap]

(xxxi) **Mohr's salt**—[*Ans.* [$(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$. As a reagent]

(xxxii) **Nessler's reagent**—[*Ans.* K_2HgI_4. Used for the identification of NH_3]

(xxxiii) **Litharge**—[*Ans.* PbO. In the preparation of lead glass]

(xxxiv) **Salt petre**—[*Ans.* KNO_3. In the preparation of HNO_3]

(xxxv) **Nitre cake**—[*Ans.* $NaHSO_4$.]

(xxxvi) **Red lead, or minium Pb_3O_4**—[*Ans.* In paint, as oxidising agent, matches, flint glass]

4. A metallic hydroxide which is used as medicine.
[*Ans.* Magnesium hydroxide $Mg(OH)_2$. Known as milk of magnesia in the medicine. Used as an antacid.]

5. A metal as a part of anion.
[*Ans.* $K_4[Fe(CN)_6]$ potassium ferrocyanide. $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$.

6. Name the main product and formula of the following reactions—

(i) Cl_2 is passed through an aqueous solutions of I_2. [*Ans.* Iodine mono chloride ICl]

(ii) A mixture of CO and Cl_2 is kept in the sun light.
[*Ans.* Carbonyl chloride or phosgene $COCl_2$]

(iii) An aqueous solution of sodium sulphite is boiled with sulphur.
[*Ans.* Sodium thiosulphate or hypo. $Na_2S_2O_3$, $5H_2O$]

(iv) Solid BaO is heated to 500°C in air. [*Ans.* Barium peroxide BaO_2]

(v) Aqueous solution of a mixture of K_2SO_4 and $Al_2(SO_4)_3$ is crystallised.
[*Ans.* Alum K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$ used in the purification of water]

7. Three reactions in which water acts as catalyst.
[*Ans.* In the bleaching action of Cl_2, in the bleaching action of SO_2 and in the combination of H_2 and Cl_2 to form hydrogen chloride]

8. Two reactions of O_3 where O_2 is not liberated.
[*Ans.* $3SO_2 + O_3 = 3SO_3$; $3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O$]

9. How would you know the presence of O_3 ?
[*Ans.* Starch iodide turns blue, paper soaked in benzedine turns brown]

10. How could you obtain N_2 from a nitrate, a nitrite and nitride ?
[*Ans.* (i) $2NaNO_3 \xrightarrow[\Delta]{} 2NaNO_2 + O_2$; $NaNO_2 + NH_4Cl = NH_4NO_2 + NaCl$; $NH_4NO_2 \xrightarrow[\Delta]{} N_2 + 2H_2O$

(ii) $NH_4NO_2 \rightarrow N_2 + 2H_2O$.

(iii) $Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3$; $3CuO + 2NH_3 = 3Cu + N_2 + 3H_2O$]

11. In which condition N_2 is liberated from HNO_3 ?
[*Ans.* $\underset{\text{hot}}{5Cu} + \underset{\text{vapour}}{2HNO_3} = 5CuO + N_2 + H_2O$]

12. What is boride ? [*Ans.* The compound which is formed by the action of a metal with boron at high temperature is called boride $3Mg + 2B = Mg_3B_2$ (magnesium boride)]

13. Which one is more stable—NH_4^+ or PH_4^+ ?
[*Ans.* NH_4^+ is more stable than PH_4^+. This is because of the fact that P is more basic than N and the hydride of P is less stable than that of N]

14. P gives PCl_3 and PCl_5 but N_2 gives only NCl_3—explain why.
[*Ans.* Nitrogen (At. wt. 7) has no vacant *d* orbitals. So it utilises its three unpaired *p* electron for the formation of bonds and gives only NCl_3. On the other hand P (At. wt. 15) has vacant *d* orbitals. So it can utilise its three unpaired *p* electrons and one 3*s* electron which is transferred from 3*s* to 3*d* orbital. As a result there are five unpaired electrons (sp^3d) to produce PCl_5]

15. How would you obtain SO_3, N_2O_5, Cl_2O_7 with the help of P_2O_5 ?
[*Ans.* $2HClO_4 + P_2O_5 = 2HPO_3 + Cl_2O_7$; $H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$;
$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$]

16. What is the absorbant of PH_3 ? [*Ans.* Bleaching powder]

17. Of the following fuels which one produces the lowest concentrations of pollutions under normal condition ? (a) coal, (b) wood, (c) natural gas, (d) petrolium ?
[*Ans.* Natural gas, because major portion of this hydrocarbon which on burning gives H_2O and CO_2. No harmful gas is evolved by its combustion]

18. Which one of the following will produce alkaline solution in their aqueous solution ? (a) NH_4^+, (b) Na^+, (c) CH_3COO^-, (d) NO_3^- ?
[*Ans.* CH_3COO^-, because CH_3COO^- is the conjugate base of a weak acid and so it will produce more OH^- ions in the aqueous solution $CH_3COO^- + H.OH \rightleftharpoons CH_3COOH + 2OH^-$]

19. What difficulty will you encounter in the ring test of nitrate with lead nitrate. How will you overcome the difficulty ?
[*Ans.* On addition of $FeSO_4$ and H_2SO_4 to the aqueous solution of $Pb(NO_3)_2$, a curdy white precipitate of $PbSO_4$ is formed and as a result ring test is not possible in case of $Pb(NO_3)_2$ or any soluble Pb salt. This difficulty may be overcome by adding H_2SO_4 to the aqueous solution of $Pb(NO_3)_2$ when a curdy white precipitate of $PbSO_4$ is formed which is filtered off. Now with the filtrate ring test is performed. The filtrate contains HNO_3

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4\downarrow + 2HNO_3$$
$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3\,Fe_2(SO_4)_3 + 2NO + 4H_2O$$
$$FeSO_4 + 5H_2O + NO = \underset{\text{brown ring}}{[Fe(H_2O)_5NO]SO_4}$$

20. What happens when lead nitrate is heated in a test tube ?
[*Ans.* When lead nitrate is heated in a dry test tube it diflagrates giving off a brown gas containing nitrogen dioxide and O_2 leaving behind a residue of PbO which is reddish brown when hot and yellow when cold.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2]$$

21. Lead Pb^{2+} is placed in Gr I as well as in Gr II of qualilative analysis—why ?
[*Ans.* $PbCl_2$ formed by the action of HCl with lead salts is partly soluble in water hence Pb^{2+} ions pass into the filtrate obtained in the Gr I i.e. it passes to Gr II.]

22. For the detection of basic radicals by flame test which acid—conc H_2SO_4 or conc HCl may be used ? [*Ans.* Conc. HCl, because the chlorides of metals are volatile where as the sulphates of metals are not volatile.]

23. What happens when a chloride is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 ?
[*Ans.* Red vapour of chromyl chloride is produced. $K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O$]

24. What happens when H_2S is passed through freshly prepared alkaline sodium nitro prusside solution ?
[*Ans.* The solution turns violet due to the formation of $Na_4[Fe(CN)_5NOS]$
$H_2S + 2NaOH = Na_2S + 2H_2O$; $Na_2S + Na_2[Fe(CN)_5NO] = \underset{\text{violet}}{Na_4[Fe(CN)_5NOS]}$

25. Why ferric sulphate is not used instead of $FeSO_4$ in the ring test ?
[*Ans.* Because the NO formed, is not absorbed by ferric sulphate to form the complex $[Fe(H_2O)_5NO]SO_4$]

26. Why NH_4Cl is added along with NH_4OH for the precipitation of Gr IIIA radicals ? [*Ans.* See page 445 (Phy Chem)]

27. In Gr II, H_2S is passed in HCl medium. What is the difficulty if H_2S is passed in alkaline medium ?

[**Ans.** In HCl medium the dissociation of H_2S decreases due to common ion effect. So under low concentration of S^{2-} ions, only the sulphides of low solubility product i.e. Gr II radicals are precipitated. In alkaline medium the concentration of S^{2-} ions increases as a result the sulphides of the next group will also get precipitated.]

28. For the precipitation of the hydroxides of Gr IIIA is it possible to use NaOH instead of NH_4OH ?

[**Ans.** No it is not possible, because Al^{3+} and Zn^{2+} will form soluble $NaAlO_2$ and Na_2ZnO_2 respectively and so their hydroxides will not be precipitated.]

29. NH_4Cl is added in Gr IIIA but not $(NH_4)_2SO_4$—explain why ?

[**Ans.** If $(NH_4)_2SO_4$ is added instead of NH_4Cl, the insoluble sulphates of Group IV (Ca^{2+}, Sr^{2+}, Ba^{2+}) will be precipitated along with the metallic radicals of Gr IIIA.]

30. Why plaster of paris becomes hard on addition of water ?

[**Ans.** Plaster of paris is converted to gypsum on addition of water, so it becomes hard.

$$2CaSO_4,(H_2O) + 3H_2O = \underset{\text{gypsum}}{2[CaSO_4, 2H_2O]}$$

31. In the preparation of gun powder KNO_3 is used.

[**Ans.** KNO_3 is not hygroscopic. It dissociates to give KNO_2 and O_2. This O_2 helps the combustion of S and C of gun powder to produce a large volume of gases for which explosion takes place.

$$2KNO_3 = 2KNO_2 + O_2, \quad S + O_2 = SO_2, \quad C + O_2 = CO_2]$$

32. What is a buffer solution ? [**Ans.** See page 428 (Phy Chem)]

33. What is the difference between (i) water of crystallisation and water of constitution ? (ii) absorption and adsorptions.

[**Ans.** (i) Water of crystallisation is the water forming part of the crystal structure of certain substances. The contents of water of crystallisation corresponds to definite chemical formulae e.g. $CuSO_4, 5H_2O$; $FeSO_4, 7H_2O$ etc. Water of constitution is not present as H_2O molecules but is formed from the H and O atoms present in a substance when it is decomposed by heat or extracted by a dehydrating agents like P_2O_5, conc. H_2SO_4.

$$C_6H_{12}O_6 + H_2SO_4 = 6C + 6H_2O + H_2SO_4]$$

(ii) Adsorption and absorption — See page 29]

34. Which one of the following is acid salt ? NaH_2PO_2, Na_2HPO_3, NaH_2PO_3, $NaOOCCH_3$. [**Ans.** NaH_2PO_3]

35. Wooden match on burning gives off a smell of burning sulphur.

[**Ans.** Match contains Sb_2S_5 which on burning evolves SO_2 and this SO_2 has got the smell of burning sulphur.]

36. Bleaching powder gives the smell of chlorine—why ?

[**Ans.** Bleaching powder evolves Cl_2 when it comes in contact with the CO_2 of air.

$$Ca(OCl)Cl + CO_2 = CaCO_3 + Cl_2\uparrow]$$

37. What is aerosol ? [**Ans.** The colloidal solution of a gas in a liquid is called aerosol e.g. fog]

38. An aqueous solution of a gas on being heated in a closed test tube yields a solid which on combustion gives off the original gas. Name the gas.

[**Ans.** The gas is sulphur dioxide. When the aqueous solution of the gas is heated in a closed tube it is decomposed to give sulphur, which on burning gives of SO_2.

$$H_2O + SO_2 = H_2SO_3, \quad 3H_2SO_3 = H_2SO_4 + S + H_2O, \quad S + O_2 = SO_2\uparrow]$$

39. What is the influence of $FeSO_4$ in the reaction of acidified KI with O_3 ?

[**Ans.** O_3 oxidises acidified KI solution to give free iodine. $2KI + 2HCl + O_3 = 2KCl + I_2 + H_2O + O_2$. If $FeSO_4$ is present in this reaction O_3 is used up in oxidising $FeSO_4$ to $Fe_2(SO_4)_3$. So there remains no excess O_3 to react with KI, as a result I_2 is not liberated.

$$2FeSO_4 + H_2SO_4 + O_3 = Fe_2(SO_4)_3 + H_2O + O_2]$$

40. What is the difference between (a) vapour density and the density of a gas.

[**Ans.** See page 53 (Phy Chem)]

41. What do you mean by two moles of electrons ? [**Ans.** 2 × 6·023 × 10^{23} number of electrons]

42. What is the differences between (a) hydrophilic and hydrophobic, (b) Hygroscopic and delequescent substance.

[**Ans.** See page 317 and 312, 314 (Phy Chem)]

43. Give a chemical reaction which shows the difference of HF from other halogen acids. [*Ans.* HF forms acidic salt like KHF_2

$HF + H^+ + F^- \rightleftarrows HF_2^- + H^+$, $KOH \rightleftarrows K^+ + OH^-$, $K^+ + HF_2^- = KHF_2$

Other halogen acids do not form acid salt of this type. AgF_2 is soluble but the other silver halides are insoluble in HNO_3.]

44. There are two samples of water. Each sample contains Mg^{2+} and Ca^{2+} ions. But one of them is parmanent hard water and other is temporary hard water. What is reason of this?

[*Ans.* The sample which contains chloride or sulphates of Mg or Ca e.g., $MgSO_4$, $CaSO_4$ or $MgCl_2$, $CaCl_2$ is permanent hard water. The sample which contains $Mg(HCO_3)_2$ or $Ca(HCO_3)_2$ is temporary hard water]

45. Arrange the following—

(a) MgO, SrO, K_2O, NiO and Cs_2O (increasing order of basic character). [*I.I.T. '91*]
[*Ans.* NiO < MgO < SrO < K_2O < Cs_2O]

(b) KCl, KBr, KI (decreasing order of solubility in water)
[*Ans.* KI > KBr > KCl]

(c) CCl_4, $MgCl_2$, $AlCl_3$, PCl_5, $SiCl_4$ increasing order of extent of hydrolysis.
[*Ans.* $CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$]

(d) NH_3, PH_3, AsH_3, SbH_3 decreasing order of stability on heating.
[*Ans.* $NH_3 > PH_3 > AsH_3 > SbH_3$]

(e) NCl_3, PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$ order of ease of hydrolysis.
[*Ans.* $NCl_3 < PCl_3 < AsCl_3 < SbCl_3 < BiCl_3$]

(f) N, P, As, Sb, Bi increasing order of +5 oxidation state
[*Ans.* Bi < Sb < As < P < N]

(g) CO_2, N_2O_5, SiO_2, SO_3 decreasing order of acidity.
[*Ans.* $SO_3 > N_2O_5 > SiO_2 > CO_2$]

(h) HF, HCl, HBr, HI increasing order of dipole moment.
[*Ans.* HI < HBr < HCl < HF]

(i) HF, HBr, HI, HCl increasing order of thermal stability.
[*Ans.* HI < HCl < HBr < HF]

(j) HF, HCl, HBr, HI increasing order of ionic character.
[*Ans.* HI < HBr < HCl < HF]

(k) HF, HCl, HBr, HI, increasing order of reducing power.
[*Ans.* HF < HCl < HBr < HI]

(l) HOCl, $HOClO_2$, $HOClO_3$, HOClO increasing order of thermal stability.
[*Ans.* HOCl < HOClO < $HOClO_2$ < $HOClO_3$]

46. Name the substances underlined—

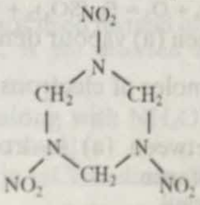
A gas obtained by the reaction of dil H_2SO_4 with a black solid, when passed through a colourless solution gives a black precipitate. The black precipitate turns white on adding a colourless liquid.

[*Ans.* Gas = hydrogen sulphide H_2S, black solid = Ferrous sulphide FeS, Colourless solution = lead acetate $(CH_3COO)_2Pb$, black precipitate = PbS, Colourless liquid = H_2O_2]

47. Give an example where mixture of two acidic solutions produce alkaline solution.
[*Ans.* $H_3BO_3 + 2KHF_2 = KBF_4 + KOH + 2H_2O$]

48. What is RDX?

[*Ans.* RDX (Research development explosive) is cyclonite. It is chemically sym-trimethylene trinitramine or hexahydro—1, 3, 5—trinitro triamine or trinitro methylene triamine.]



• QUESTIONS •

H.S. & JT. ENT.

H.S. CHEMISTRY : 1991

First Paper

Group – A

(Answer any *FOUR* questions)

1. (a) State Avogadro's hypothesis. What was the necessity for its formulations ?

(b) Prove that the molecular weight of a gas is twice its vapour density.

(c) A compound of carbon, hydrogen and oxygen contains $C = 40\%$, $H = 6{\cdot}67\%$. When the compound is vaporised, its vapour density is found to be 2·813 times that of oxygen. Find the empirical and molecular formulae of the compound. 3 + 3 + 4

2. (a) State Dulong and Petit's law. How is this law applied to find out the atomic weight of an element ? What are the limitations of this method ?

(b) The chloride of a metal contains 20·2% metal. The specific heat of the metal is 0·224. Calculate the exact atomic weight of the metal. Write down the molecular formula of the chloride of the metal. 2 + 2 + 2 + 4

3. (a) The chemical reaction that takes place during the manufacture of sulphuric acid by contact process is as follow :
$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) + 45$ K cals. Explain the effects of changes of pressure and temperature on this reaction after stating the necessary principle.

(b) Specific gravity of 61 per cent by weight of Nitric acid is 1·41. Determine its normality. 6 + 4

4. (a) State Faraday's Laws of electrolysis.

(b) When 0·5 ampere of electricity is passed through a dilute solution of silver nitrate for 5 minutes, 0·2015 gm. of silver is deposited. Find out the electrochemical equivalent of Silver. 4 + 5 + 1

(c) What is a Faraday ?

5. (a) What do you understand by saturated and unsaturated solutions ?

(b) What is solubility ? What is its difference from solubility product ?

(c) Write notes on (i) Colloidal solution (ii) Formal solution. 2 + 4 + 2 + 2

6. (a) Deduce the equation $PV = nRT$.

(b) Why R is called universal gas constant ?

(c) 0·64 gm. of a gas occupies 224 ml. at 76 cm. pressure and at 273K temperature. At what temperature one gramme of the gas will occupy one litre at one atmosphere pressure ? 4 + 2 + 4

Group – B

(Answer any *FOUR* questions)

7. Write with equations what happens when : (any *four*)

(a) White phosphorous is heated with concentrated solution of potassium hydroxide.

(b) Water is gradually added to a mixture of red phosphorous and iodine.

(c) Ozone is allowed to react with acidic solution of potassium iodide.

(d) A mixture of aqueous solution of ammonium chloride and sodium nitrite is heated.

(e) Iodine is allowed to react with sodium thiosulphate solution. 2½ × 4

8. (a) How with the help of Kipp's apparatus a ready supply of hydrogen sulphide gas is obtained in a laboratory ? Explain it with a sketch.

(b) Explain what happens when hydrogen sulphide is passed into dilute hydrochloric acid solution containing cupric chloride and zinc chloride. 7 + 3

9. (a) Name the main constituents of coal gas.

(b) What are the by-products obtained in the preparation of coal gas ?

(c) How pure carbon monoxide is prepared in the laboratory ?

(d) How will you prove that carbon di-oxide contains carbon ? 2 + 2 + 4 + 2

10. (a) Describe the manufacture of nitric acid by Oswald process.

(b) Write with equations, the reactions of nitric acid with each of the following substances :
(i) Ferrous sulphate (ii) Magnesium. 6 + 2 + 2

11. (a) What happens when orthoboric acid is gradually heated ?

(b) How orthoboric acid is detected ?

(c) Why aqueous solution of borax is alkaline ?

(d) How will you prove oxidizing property of sulphur di-oxide and reducing property of carbon monoxide ? 3 + 2 + 2 + 3

12. Explain : (any *four*)

(a) Fluorine cannot be prepared by electrolysing aqueous hydrofluoric acid solution.

(b) Concentrated sulphuric acid is not used in the preparation of hydrogen peroxide.

(c) Orthophosphoric acid behaves as a dibasic acid.

(d) Ammonia is more basic than phosphine.

(e) Graphite conducts electricity but diamond does not conduct electricity. 2½ × 4

JT. ENT. CHEMISTRY : 1991

Time—3 hours Full marks—100

Attempt All questions

1. (i) What is matte ? Discuss the reactions involved in the extraction of copper from matte.

(ii) A solution containing 3 moles of patassium hydroxide is added to a solution containing 2 moles of phosphoric acid. Water is evaporated. What is the composition of the crystals precipitated ? 3+2

2. (i) Describe with equation what happens when

(a) Potassium cyanide solution is mixed with copper sulphate solution.

(b) Borax is heated on a platinum loop.

(ii) Rain water during thunderstorms contains a small amount of nitric acid. By what reactions is it formed ? 4+1

3. (i) How can salts of iron (II) and iron (III) be differentiated if both are soluble in water ?

(ii) Write down the equations for reactions by which the following conversions can be realised :

$$Fe_2O_3 \rightarrow Fe \rightarrow FeCl_2 \text{ (anhydrous)} \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow Fe_2O_3$$

(iii) A small diamond was alloyed with iron. What products were formed ? How was the chemical nature of diamond disclosed by this experiment ? 1+3+1

4. Gas evolved by treating sodium sulphide with water is passed into ammoniacal zinc chloride solution. What is the colour and composition of the precipitate ? What happens if the precipitate is treated with hydrochloric acid followed by sodium hydroxide solution ? 5

5. How would you distinguish between— 5

(1) Chlorine (g) and Bromine (g). (2) Ozone and Oxygen. (3) Nitrous oxide and Nitric oxide. 2+1+2

6. (i) To restore the original colour of old oil paintings hydrogen peroxide is used.—Explain the reason with chemical equation.

(ii) Of the two gas jars one contains bromine vapour and the other nitrogen dioxide. How can you determine by a simple experiment which jar contains which gas ? 2+3

7. How will you distinguish between :

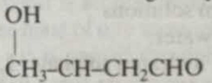
(a) Ammonia and Phosphine.

(b) Hydrogen peroxide and Ozone.

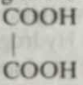
(c) Chlorine and Iodine.

(d) Red Phosphorus and White Phosphorus. 1+1+1+1

8. (i) Name the following compounds according to I.U.P.A.C system : 2+1

(a) 

$\overset{\text{OH}}{\overset{|}{CH_3-CH-CH_2CHO}}$

(b) 

$\begin{array}{c}COOH\\ |\\ COOH\end{array}$

(ii) Write the structures and names of two different compounds having the same molecular formula C_3H_6O belonging to two different homologous series. Mention one reaction which is applicable to both the compounds. Mention one reaction of each compound which is not given by the other.

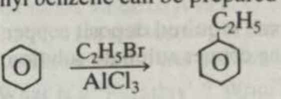
9. (i) How would you prepare the following ? 2+2

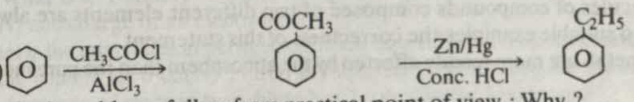
(a) Acetylene from methane and methane from acetylene.

(b) Aniline from benzene and benzene from aniline.

(ii) A solid compound having the molecular formula C_6H_6NCl is soluble in water and the aqueous solution turns blue litmus red and produce curdy white precipitate with aqueous $AgNO_3$. When aqueous $NaNO_2$ added to the aqueous solution of the compound and the resulting solution is poured into a solution of β-napthol is aqueous NaOH, a scarlet reprecipitate is obtained. Identify the compounds giving proper argument.

10. (i) Ethyl benzene can be prepared by the following two methods :

(a) 

(b) 

Which method would you follow from practical point of view ; Why ?

(ii) How can you separate ethyl alcohol and acetone from a mixture containing the two ? 2+1

3

11. How would you distinguish between :

(i) Formaldehyde and acetaldehyde. (ii) Chlorobenzene and benzylchloride. (iii) Methyl alcohol and ethyl alcohol.

12. How would you convert :

(a) Ethyl alcohol to methyl alcohol. (b) Sodium formate to sodium oxalate. (c) Formic acid to acetic acid.

13. (i) In his periodic table Mendeleef placed cobalt (at. wt. 58.9) before nickel (at. wt. 58.7) How this apparent anomaly has been justified in modern periodic table ?

(ii) Write down the electronic configuration of the element having At. no. 21. Name two other elements of the same series to which this element belongs. Why do they belong to the same series ?

(iii) Nitrogen forms NCl_3 only, while phosphorus can form both PCl_3 and PCl_5–Explain. 1+3+1

14. (i) 'α' particles will do more damage inside the body than 'β' particles.—Why ? Is it also true when the body is exposed to the external source of such radiations ?

(ii) Can γ-ray emerge from a natural radioactive element before the emission of α and β-particles ?

(iii) Complete the following reactions :

(a) ${}^4_2He + {}^{14}_7N \rightarrow ? + {}^1_1H$ (b) ${}^{226}_{88}Ra \rightarrow ? + {}^{222}_{86}Rn$ 2+1+2

15. (i) You find bottles marked "Conc. H_2SO_4" "Conc. HCl" as also "Dil. HCl", "Dil. H_2SO_4" in the reagent racks of your laboratory. What are the approximate strength in normalities of these acids ?

(ii) How can you prepare 360 ml of that "Dil. H_2SO_4" from the "Conc. H_2SO_4" ?

(iii) A piece of aluminium weighing 2.7 g is heated with 75.0 ml of sulphuric acid (sp. gravity 1.18, containing 24.7% H_2SO_4 by weight). After dissolving the metal carefully the volume of the solution is made upto 400 ml by adding water. Determine the molarity of sulphuric acid present in the prepared solution. [Al = 27, S = 32] 1+1+3

16. (i) Predict whether the following substances will form solutions ?

(a) Methane and water. (b) Hydrogenbromide and water.

(ii) 1.0 gm of a metal (at. wt. 56) produces 4.9642 gm. of hydrated sulphate. 1.0 gm of this hydrated sulphate on heating liberates 0.4532 gm of water. What is the simplest formula of the hydrated sulphate ? 2+3

17. (i) Equal weights of two substances A & B are taken. The ratio of their atomic weights is 2:3.

(a) What is the ratio of molecules in the equal weights of these substances ?

(b) If the substances are vapourised what will be the ratio of their volumes under the same conditions of temperature and pressure ?

(ii) A 2-litre glass vessel contains nitrogen and water vapour in equimolar proportion at 10^{-3} mm. Hg pressure and 303K temperature.

(a) Find out the total number of moles of nitrogen and water vapour present.

(b) Find out the total mass of the gas mixture.

(c) What will be the total mass of the gas mixture if it is cooled to 50°C. 2+3

18. (i) What do you mean by "electrochemical equivalent" and "chemical equivalent" of an element ? 2+3

(ii) Determine the amount of electricity in coulomb required deposit copper of thickness 10^{-3} cm. on a plate having area of 100 sq.cm. using copper sulphate solution. [Density of copper is 8.94 gm/cc, Cu=63.5]

19. (i) Molecules of compounds composed of two different elements are always polar—discuss with two suitable examples the correctness of this statement.

(ii) Impure metals are more readily affected by the atmosphere than the pure metals—Why ? 2+1

20. (a) Name the respective groups and periods of the elements having atomic no. 18 and 26. 1+1+1

(b) What would be the possible valencies of those elements ?

(c) State giving reason, why argon of atomic wt. 39.94 has been rightly placed before potassium of atomic weight 39.01 in the periodic table.

21. How would you show that nitric acid contains oxygen. 1

22. The inert gases are monatomic. Why ? 1

23. What property of carbon allows it to form long carbon-chain ? 1

24. The aqueous solution of a gas produces a solid when heated in a sealed tube. When the solid is burnt in air the original gas is obtained. Identify the gas. 1

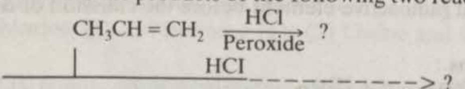
25. Write the structure and name of the simplest alkyne which does not form precipitate with ammoniacal cuprous chloride solution.

26. What is meant by—molecular mass of ammonia is 17 a.m.u. ? 1

27. The rate of evaporation of water increases with decrease in pressure and increase in temperature.—Why ? 1

28. Give examples of two colourless gases which form a white solid on mixing. 1

29. What are the products of the following two reactions ?



$$CH_3CH=CH_2 \xrightarrow[\text{Peroxide}]{HCl} ?$$

$$CH_3CH=CH_2 \xrightarrow{HCl} ?$$

30. What is the mass of 1 millimole of ammonia ? How many numbers of molecules of ammonia are present in it ? 1

H.S. CHEMISTRY : 1992

First Paper

Group – A

(Answer any *FOUR* questions)

1. (a) What is atomic mass unit (a.m.u.) ? Atomic weight of nitrogen is 14·007 a.m.u. What is the mass of one atom of nitrogen in grams ?

(b) H_2 gas is passed through one gram each of two heated oxides of *M*. 0·1258 gm and 0·2263 gm of water are produced respectively. Show that these data are in conformity with a Law of Chemical Combination. What is the law and who discovered the law ?

(c) If the equivalent weight of a metal [*M*] be *x* and the formula of its oxides be M_mO_n, show that the atomic weight of [*M*] is $\frac{2xn}{m}$. 3 + 4 + 3

2. (a) Show that at standard pressure and temperature the gm-molecular volume of gases usually is 22·4 litres.

(b) State Mitscherlich' Law of isomorphism. Cite two examples.

(c) A certain hydrocarbon required 5 times its volume of oxygen for complete combustion and the resultant gas mixture on being shaken with caustic potash solution showed a contraction equal to thrice the volume of the hydrocarbon taken. Find the formula of the hydrocarbon.

(All volumes have been measured at same temperature and pressure) 3 + 3 + 4

3. (a) State Boyle's Law. Express the law with the help of two graphs.

(b) Find out the value of *R* in C.G.S. unit.

(c) At 100°C a closed vessel of 1500 ml capacity contains 0·4 gm O_2 and 0·6 gm H_2. What is the total pressure of the gas mixture in the vessel ? 4 + 2 + 4

4. (a) What is a 'Faraday' ? Write down the equation relating Faraday (F), Avogadro number (N) and charge of an electron (e).

(b) What is the interrelation between chemical equivalent and electrochemical equivalent ?

(c) What volume of 0·05(N) H_2SO_4 is required to neutralise the alkali produced after passing 0·4 ampere of electricity in dilute NaCl solution for 5 minutes ?

(d) Name an indicator which can be used in the titration of dilute acetic acid with dilute caustic soda solution. Give reason for your choice. 2 + 1 + 4 + 3

5. (a) State Graham's Law of diffusion. How molecular weight of a gas can be determined with the help of this law ?

(b) What is meant by chemical equilibrium ? What is equilibrium constant ? How Le Chatelier's principle is used in the commercial preparation of ammonia ?

(c) An aqueous solution of borax is alkaline. Explain. 4 + 4 + 2

6. (a) What is meant by 'Solubility of KNO_3 at 40°C is 65' ?

(b) What is solubility curve ? Explain solubility curve of $Na_2SO_4, 10H_2O$.

(c) Write note on dialysis. 2 + 4 + 4

Group – B

(Answer any *FOUR* questions)

7. (a) Give a method with necessary chemical equation for preparation of hydrogen peroxide commercially. What do you mean by "10 Volume H_2O_2" ?

(b) What are the causes of temporary and permanent hardness of water ? How can you prepare de-ionised water ?

(c) Describe briefly the large scale preparation of hydrogen from water gas. 4 + 3 + 3

8. (a) What is the basic principle for the preparation of ammonia in the laboratory ? Give one example with equation.

(b) How would you prove the presence of nitrogen and hydrogen in ammonia ?

(c) What is Nessler's reagent ? What visible changes are noticed when ammonia gas is passed through Nessler's reagent ?

(d) What is 'Oleum' ? Mention one use. 3 + 2 + 3 + 2

9. (a) Illustrate with one equation in each of the following :
  (i) Reducing property of iodine.
  (ii) 'Additive property' of carbon monoxide.
  (iii) Reducing property of H_3PO_3.

(b) How would you separate the gases from the following gas mixtures ?
  (i) CO and CO_2
  (ii) NO and N_2O
  (equations are not required)

(c) Hydroflouric acid is weaker than hydrochloric acid. Explain. 3 + 4 + 3

10. (a) Give necessary chemical equations for the preparation of phosphorus from phosphorite mineral.

(b) How P_4O_{10} is related to HPO_3 and H_3PO_4 ? Give necessary chemical equations.

(c) What is 'superphosphate of lime' ? What is its importance ?

(d) "PCl_3 is a covalently bonded liquid ; when added to water, the solution conducts electricity." Explain. 3 + 2 + 2 + 3

11. Explain : (any *four*) 2½ × 4

(a) The colour of concentrated nitric acid is usually yellowish.
(b) Mobility of mercury is lost in contract with ozone.
(c) N_2O is supporter of combustion and combustion occurs more readily than in air.
(d) "Tajmahal" is susceptible to atmospheric damage.
(e) A colourless transparent substance is formed on heating borax.
(f) The presence of carbon monoxide in air is more harmful than that of carbon dioxide.

12. What happens when : (any *four*) 2½ × 4
  (a) Phosphine is passed into the solution of $CuSO_4$.
  (b) Chlorine gas is passed through HBr solution.
  (c) Sand is treated with hydrofluric acid.
  (d) H_2S is passed into acidified solution of $K_2Cr_2O_7$.
  (e) Solid boric acid is heated with methanol.
  (f) Carbon dioxide gas is passed into water under high pressure.
  (Give equations)

JT. ENT. CHEMISTRY : 1992

Time—3 Hours *Full Marks—100*

Attempt All *questions.*

1. (a) A sample of mixture of NaCl and NaBr weighing 0.1809 gm is treated with $AgNO_3$ solution to give 0.3715 gm of precipitate. Calculate the content of NaCl and NaBr in the mixture. [Na=23, Cl=35.5, Br=79.9, Ag=107.87] 2

(b) Explain the following reactions with an example for each : 1½+1½
  (i) Disproportionation Reaction, (ii) Rearrangement Reaction.

2. (a) Do the density and vapour density of a gas depend on temperature and pressure ? Explain in two to three sentences.

(b) Is moist air heavier than dry air ? Explain.

(c) 2 g of hydrogen and 2 g of deuterium are introduced into a 10 liter evacuated cylinder at 300 K and sealed. Find the pressure. Will the pressure be the same if the container was cubical of the same capacity ? 2+1+2

3. 25 ml of 6% Na_2CO_3 solution was made up to 250 ml. 25 ml of this diluted solution requires 30.1 ml dilute H_2SO_4 in presence of methyl orange as indicator.

(a) Calculate the normality and pH of the acid solution.

(b) Determine the amount of $Na_2SO_4, 10H_2O$ to be obtained from neutral solution.

(c) If phenolphthalein be used as indicator, calculate the volume of dilute H_2SO_4 required for neutralisation and also the amount of different salts remained in the solution. 5

4. (a) What is an aerosol ? Give two examples.

(b) Why do industrial chimneys emitting smokes have charged plates ?

(c) Arrange H_2CO_3, glucose, NaCl and HCl solutions (each 0.1 M) in order of increasing molecular conductivity.

(d) Is a solution of borax-neutral ? 2+1+1+1

5. (a) How the atomic radii of the elements along a period changes ?

(b) Comment on the placement of hydrogen in GrIA.

(c) What is the importance of zero group elements in the periodic table ?

(d) Covalency possess directional properties but electrovalency has no such characteristic. —Why ?

(e) Name a compound which contains an atom with less than eight electrons in the outermost shell. 1+1+1+1+1

6. (a) Find the relative rate of diffusion of $^{235}UF_6$ and $^{238}UF_6$ in the gaseous state. [F=19]

(b) When 2 gms of gas 'M' is introduced into an empty flask at 30°C, its pressure becomes 1 atmosphere. Now, if 3 gms of another gas 'N' is introduced in the same flask at the same temperature, its total pressure becomes 1.5 atmosphere. Find the ratio of the molecular weights of the two gases M and N. 2+3

7. (a) What is the mass of a proton in gm ?

(b) Do you agree with the statement "Atoms of the same element have same mass, while atoms of different elements have different mass" ? Explain.

(c) Is it injurious to health to take a bath in heavy water ? Explain. 1+1+1

8. (a) Write down the electronic configuration of P^{-3} ion.

(b) Find the volume of oxygen at STP that can be obtained by the complete decomposition of 30 c.c. of 20 volume hydrogen peroxide.

(c) Write the electron dot structure of Ozone. 1+1+1

9. What happens when

(a) NO_2 gas is passed into conc. H_2SO_4 ?

(b) H_2S is passed into freshly prepared alkaline sodium nitroprusside solution ?

(c) pH_3 is passed into an aqueous solution of bleaching powder ?

(d) Na_2CO_3 solution was added to $FeCl_3$ solution ?

(e) Ammonia gas is reacted with Cl_2 gas ? 1+1+1+1+1

10. (a) The reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is exothermic. Why is then synthesis of ammonia is carried out at higher temperature ?

(b) How can you convert ammonia into ammonium sulphate without using sulphuric acid ? Give equation only.

(c) Why is nitrous oxide collected over hot water, while nitrogen can be collected over water at room temperature ?

(d) Write an equation for the reaction between phosphorus and hot concentrated nitric acid. 1+1+1+2

11. (a) Why does bleaching powder give out a smell of chlorine ?

(b) Why do we feel a pungent smell just at the moment when a match stick starts burning ?

(c) If you are given two identical sealed bottles filled with concentrated H_2SO_4 and concentrated HCl, how can you identify them without opening the bottles ?

(d) Why is white phosphorus more reactive than red phosphorus ? How is white phosphorus preserved ?

(e) Iodine is very slightly soluble in water, but it is readily soluble in a concentrated KI solution.—Why ? 1+1+1+1+1

12. (a) How would you achieve interconversion between—
(i) Red phosphorus and white phosphorus ; (ii) Rhombic sulphur and Monoclinic sulphur ; (iii) Ammonia and Nitric Oxide. 1+1+2

(b) Why graphite is a conductor of electricity and diamond is not ? 1

13. (a) What is the main constituent of slag in the blast furnace during the production of iron ?

(b) What is thermit process ?

(c) Write the equations for the reactions taking place during the roasting and smelting of zinc blende. What is galvanised iron ?

(d) What is the formula of the brown compound formed in the ring test for nitrate ? Can you use ferric sulphate in this test ? 1+1+2+1

14. How would you identify the following ions in presence of one another :
(a) Bromide (Br^-) and Iodide (I^-), (b) Ca^{+2} and Mg^{+2}.
Write down the reactions involved. 2+2

15. Compound (A) gives out a pungent smell on boiling with NaOH solution and a red litmus paper turns blue on holding over the test tube. A solution of (A) liberates an odourless gas (B) on gentle heating. A solution of (A) gives a transient blue solution on the addition of dilute sulphuric acid ; then it emits a brown gas (C). Identify (A), (B) and (C) giving reasons. 4

16. An organic compound containing carbon, hydrogen and oxygen contains 64.9% of carbon and 13.5% of hydrogen. When vaporised in a Victor Meyer apparatus, 0.185 g of it displaces 56.0 c.c. of air at STP. The compound may be easily prepared from ethanol in one step. Write down the name (in IUPAC system) and structure of the compound [C, 12]. Can you prepare it from ethene ? 5

17. (a) Two isomeric organic compounds A and B have the molecular formula $C_4H_8O_2$. A on hydrolysis gives methyl alcohol and an acid C which on decarboxylation gives ethane, whereas B on hydrolysis gives ethyl alcohol and an acid D which on reduction gives ethyl alcohol. Identify the compounds A, B, C and D. 3

(b) How would you prepare B in the laboratory ? 2

18. Write the products and name them : 1+1+1+1+1

(a) Toluene $\xrightarrow[\text{Boiling Condition}]{Cl_2}$ Ⓐ

(b) Toluene $\xrightarrow[Fe]{Cl_2}$ Ⓑ + Ⓒ

(c) Nitrobenzene $\xrightarrow[H_2O]{\text{Zn-NaOH}}$ Ⓓ

(d) Nitrobenzene $\xrightarrow[H_2O]{\text{Zn-}NH_4Cl}$ Ⓔ

(e) Benzene $\xrightarrow[\text{Sunlight}]{Cl_2}$ Ⓕ

19. (a) A leaking LPG cylinder gives out an intense smell. Is it due to butane ?
(b) What is the main product when excess of chlorine is passed into boiling toluene ?
(c) Which of the following are free radicals ? $(CH_3)_3C^+$, CH_3, Cl^- and $(CH_3)_3C$. 3

20. How would you prepare : (a) Dimethyl ether from methyl alcohol ; (b) Chloroform from acetaldehyde ; (c) Ethyl alcohol from glucose ? 1+1+1

21. Name a gaseous compound excepting oxygen which helps ignition. 1

22. One gram of radio-active material with half-life period two years is stored for six years. How much of the material remains intact ? 1

23. What is azeotrope ? Give and example. 1

24. Among H, C, Si, O, Cl, N and S which one is most electronegative ? 1

25. Which of the oxides Al_2O_3, SO_2, SO_3, P_4O_{10} and CO is most acidic ? 1

26. What is the charge carried by one mole of $P_2O_7^{4}$ ion ? Give units also. 1

27. Which of the compounds $SnCl_2$, $SnCl_4$, SnF_2, SnF_4 and $SiCl_4$ is least covalent ? 1

28. Which of the following is acid salt ?
NaH_2PO_2, Na_2HPO_3, NaH_2PO_3 and $NAOOCCH_3$. 1

29. Complete the following equation (for the nuclear reaction) :
$^{9}_{4}Be + ^{4}_{2}He \rightarrow ? + ?$ 1

30. Write down the name and structural formula of a trihydric alcohol having domestic use. 1

H.S. CHEMISTRY : 1993

First Paper

Group – A

(Answer any *FOUR* questions)

1. (a) State the law of multiple proportion. Give one example.

(b) What is the difference between a true solution and a colloidal solution ?

(c) What is meant by 'water of crystallisation' ? Give two examples.

(d) Is the solubility of sugar in a cup of water the same at Calcutta and Darjeeling ? Give reasons for your answer.

7·6 gms of a saturated solution of sugar at 20°C contains 5·1 gm of sugar. Determine the solubility of sugar at 20°C. 3+2+2+3

2. (a) What do you understand by 'mole' ?

(b) How many atoms of hydrogen and oxygen are there in 0·09 gm of water ?

(c) A baloon of 1000 litre capacity is to be filled with hydrogen gas at 30°C and 750 mm pressure. How many grams of iron are required to produce the necessary amount of hydrogen gas ?

(d) What is meant by 'reversible reaction' and 'chemical equilibrium' ? 1+2+4+3

3. (a) Define 'equivalent weight'.

Is the equivalent weight of iron same in ferrous oxide and ferric oxide ? (Atomic weight of iron is 55·85)

(b) Dulong and Petit's Law is an approximate one, yet correct atomic weight can be obtained using it.—Explain.

(c) 5·01 gm of a metallic oxide on reduction by hydrogen produce 4·41 gm of the metal. The specific heat of the metal is 0·055. What is the atomic weight of the metal ?

(d) Give an example of 'isomorphous crystal'. 3+2+4+1

4. (a) What is meant by 'absolute zero' and 'ideal gas' ?

(b) Name one unit of the 'universal gas constant' and calculate its value in that unit.

(c) A quantity of oxygen occupies a volume of 500 ml. at 27°C. At which temperature does the volume become double ? (pressure remains the same)

(d) At constant temperature and pressure, what is the relation between the rate of diffusion of a gas and its molecular weight ? 2+2+4+2

5. (a) Give one example of each of the following :

(i) basic salt, (ii) complex salt, (iii) amphoteric oxide, (iv) acid-base indicator.

(b) State and explain whether the aqueous solution of the following salts are acidic or basic or neutral to litmus :

(i) sodium bicarbonate, (ii) sodium chloride, (iii) ammonium chloride, (iv) ammonium carbonate.

(c) Express the concentration of the following solutions in gm/litre :

(i) 0·05 (N) sodium carbonate solution, (ii) 0·2 (M) sulphuric acid solution.

(d) 30 ml of 0·2 (N) sulphuric acid and 20 ml 0·3 (N) sulphuric acid are mixed together. What is the strength of the resulting acid ? 2+4+2+2

6. (a) Explain with reasons :

(i) Same products are obtained when dilute sodium hydroxide solution and dilute sulphuric acid are electrolysed with platinum electrodes.

(ii) Pure liquid hydrogen chloride and pure water are both bad conductors of electricity, but an aqueous solution of hydrogen chloride is an electrolyte.

(iii) When copper sulphate is electrolysed with copper electrodes, the anode decreases in weight.

(b) 0·2964 gm of copper is deposited at the cathode when a current of 0·5 ampere passes through a copper sulphate solution for 30 minutes. Find out equivalent weight and atomic weight of copper. 6+4

Group – B

(Answer any *FOUR* questions)

7. (a) What the following substances are chemically ?
(i) dry ice, (ii) aqua regia, (iii) borax, (iv) nitrolim.

(b) Give example of two gases combining to give a solid product.

(c) There are two bottles containing dilute sulphuric acid and dilute hydrochloric acid. State one test for each by which they may be identified.

(d) Give example of a 'bleaching agent' and a 'nitrogenous fertiliser'. 2+2+4+2

8. (a) Prove with example :

(i) Hydrogen peroxide acts as an oxidising agent, as a reducing agent and also as a mild acid.

(ii) Nitric acid is a powerful oxidising agent.

(iii) Sulphur dioxide acts as a reducing agent.

(b) There is a mixture of carbon dioxide and carbon monoxide gas. How can you

(i) convert the gas mixture fully to carbon dioxide ?

(ii) convert the gas mixture fully to carbon monoxide ?

(iii) remove carbon dioxide from the gas mixture ?

(c) What do you understand by saying that the hardness of the water of a particular tubewell is 300 p.p.m. ? 5+3+2

9. Explain why : (any *four*)

(a) Hydrogen sulphide is not prepared by the action of nitric acid on ferrous sulphide.

(b) Dilute sulphuric acid is not used in the preparation of carbon dioxide from limestone.

(c) Ammonia gas cannot be dried by phosphorous pentoxide.

(d) Manganese dioxide is used in the preparation of oxygen from potassium chlorate.

(e) In the laboratory preparation of hydrogen peroxide, hydrated barium peroxide rather than the anhydrous variety is used. 2½×4

10. Write with equations what happens when : (any *four*)

(a) Chlorine gas is passed through an iodine solution in water.

(b) Sulphur is added to boiling concentrated sulphuric acid.

(c) Nitrogen gas is passed over hot calcium carbide.

(d) White phosphorous is boiled with caustic soda solution.

(e) Hydrogen sulphide is passed into ferric chloride solution in presence of hydrochloric acid. 2½×4

11. How do you prepare ? (any *four*)

(a) Anhydrous hydrofluoric acid.

(b) Hydrogen gas from an alkali.

(c) White phosphorous from red phosphorous.

(d) Phosphoric acid from bone ash.

(e) Chlorine from sodium chloride. 2½×4

12. (a) Write down the physico-chemical principle involved in the synthesis of ammonia gas by Haber's process.

(b) How is ammonia converted to nitric acid by Ostwald process ?

(c) How do you identify nitric acid ?

(d) How would you prepare dilute sulphuric acid from concentrated sulphuric acid ? 4+3+2+1

JT. ENT. CHEMISTRY : 1993

Attempt All questions

1. (a) Distinguish between 'saturated solution' and 'supersaturated solution'.

(b) Define solubility product for a sparingly soluble salt.

(c) Decide if a precipitation occurs on the mixing together the 10 ml of 0·02 N solution of $CaCl_2$ and 5 ml of 0·1 N solution of K_2CrO_4 ($SP_{CaCrO_4} = 2{\cdot}3 \times 10^{-2}$). 1+1+3

2. (a) A solution of 1 M $CuSO_4$ is electrolysed between Cu-electrodes by a current of 10A for 965 secs at 25°C. What changes occur at both the electrodes and in the solution ? 1+1+1

(b) Describe the changes that would occur if the electrolysis is carried out as in (a) with 2 M $CuSO_4$ solution at 50°C. 1

(c) Describe the changes that would occur (at electrodes and in solution) if the electrolysis is carried out, as in (a) using both the electrodes as Pt-electrode. [At. wt. of Cu = 63·5] 1

3. (a) A mixture of Na_2CO_3 and $NaHCO_3$ has a mass of 22·0 gm. Treatment with excess HCl solution liberates 6·00 litre CO_2 at 25°C and 0·947 atm. Determine the % of Na_2CO_3 in the mixture.

(b) The volume of one atom of a metal M is $1{\cdot}66 \times 10^{-23}$ c.c. find the at. wt. of M. (Given density of M = 2·7 gm/c.c.) 4+1

4. Distinguish between : 1+1+1+1+1

(a) Water of Crystallisation and Water of Constitution,

(b) Isotope and Isomer,

(c) Adsorption and Absorption,

(d) Homogeneous Equilibrium and Heterogeneous Equilibrium,

(e) Hydrophobic and Hydrophilic.

5. (a) (i) What will be the nature of graph if P is plotted against V for a given mass of gas at constant temperature ?

(ii) How can the graph be converted to a straight line parallel to the P-axis ? Give reason.

(b) Striking a wooden match involves the combustion of P_4S_3 to produce a white smoke of P_4O_{10} and gaseous sulphur dioxide, SO_2. Calculate the volume of SO_2 that is formed at 27° and 770 mm Hg pressure from the combustion of 0·0546 g P_4S_3 [P = 31, S = 32, O = 16].

(c) How many atoms of carbon has a young man given his bride-to-be if the engagement ring contains a 0·50 carat diamond ? There are 200 mg in a carat. 1+2+2

6. (a) What are the compositions of nuclei of $^{35}_{17}Cl$ and $^{35}_{17}Cl^-$?

(b) There are two naturally occurring isotopes of hydrogen ($^1H > 99\%$ and $^2H < 1\%$) and two of chlorine (^{35}Cl 76% and ^{37}Cl 24%) :

(i) How many different HCl molecules can be formed from these isotopes ?

(ii) List the molecules in order of decreasing relative abundance.

(c) Only two isotopes of copper are present in naturally occurring copper : 63_{Cu} (62·9298 a.m.u.) and ^{65}Cu (64·9278 a.m.u.). Calculate the percentage composition of naturally occurring copper (atomic mass of copper 63·546 a.m.u.). 1+2+2

7. (a) What is buffer solution ? What is the pH of an equimolar mixture of sodium acetate-acetic acid buffer solution ?

(b) How will the degree of dissociation of a 0.1 M solution of acetic acid change if 8.2 gm of anhydrous sodium acetate are added to one litre of the solution ? (K_{dis} of acetic acid is 1.8×10^5). 1+2

8. (a) How would you use solubility curve for the separation of sodium chloride and potassium chloride present in a mixture of the two ?

(b) Suggest simple laboratory tests by which you could determine if a solution is unsaturated, saturated or supersaturated. Explain why your suggestions would distinguish between the different classifications. 2+1

9. How would you convert : 1+1+1+1+1

(i) $CaCO_3 \rightarrow CO$, (ii) $Pb(NO_3)_2 \rightarrow N_2$, (iii) Water gas→$CO_2$, (iv) $S \rightarrow H_2S$, (v) Gypsum→ Plaster of Paris.

10. Explain why : 1+1+1+1+1

(a) Sodium is kept under kerosene.

(b) Potassium nitrate is used in gunpowder.

(c) Plaster of Paris hardens on addition of water.

(d) Dike other halojens fluorine cannot form addition compounds with unsaturated organic compounds.

(e) Lead ions come in Group I and in Group II of group analysis of metal ions.

11. (a) How can you prepare red phosphorus from calcium phosphate ?

(b) In an industrial production of hydrogen first steam is passed over red hot iron and then water gas is passed. What are the functions of (i) steam, (ii) water gas ? 3+2

12. What happens when : 1+1+1+1+1

(a) Cuprous oxide is heated with dimethyl sulphate at 160°.

(b) Sodium bicarbonate solution is added to a solution of fine sulphate.

(c) Aluminium chloride hexahydrate is heated.

(d) Bleaching powder solution is added to hot lead acetate solution.

(e) When sulphur dioxide gas is passed through a solution of ferrous chloride containing concentrated hydrochloric acid.

13. (a) State the electrolyte, electrodes and the condition for extraction of Al by electrolysis. Give reaction.

(b) Give the reactions taking place during the reduction of Fe_2O_3 in the blast furnace.

(c) Which of the following contains more carbon ?

Cast Iron, Steel. 2+2+1

14. (a) How do you separate the contents from the mixture ? 1+1+1

(i) CO and CO_2, (ii) N_2 and NH_3, (iii) A black powder containing carbon and MnO_2.

(b) What are superphosphate of lime and soda lime ? 1

15. (a) What will be the observation if lead nitrate is heated in a dry test tube ?

(b) What difficulty will you encounter in the ring test of nitrate with lead nitrate ? How will you overcome the difficulty ?

(c) How can you distinguish between sodium hydrogen carbonate and sodium hydrogen sulphite ? 1½+1½+1

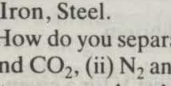
16. An organic compound A, $C_5H_{12}O$ reacts with Na with evolution of H_2. A on oxidation yields B, $C_5H_{10}O$. B reacts with I_2 in presence of KOH giving a yellow precipitate. A on treatment with ooncentrated H_2SO_4 at 170°C yields C, C_5H_{10}. C on oxidation with hot $KMnO_4$ solution yields D, C_3H_6O and E, $C_2H_4O_2$. Calcium salts of E on heating given D. Identify the compounds A, B, C, D and E with explanation. 5

17. (a) How are the following conversions accomplished ? 3

(i) Ethanol → 1, 1-Diethoxyethane

(ii) $CH_3COCH_3 \rightarrow CH_3C\equiv CH$

(iii)



(b) How are the following removed ? 2

(i) Small amount of ether peroxide present in ether.

(ii) Small amount of thiophene present in benzene.

18. How would you obtain ? 1+1+1+1+1

(a) Phenol from Benzene,(b) Salicylic acid from Phenol, (c) Benzaldehyde from Toluene, (d) Iodobenzene from Aniline, (e) Ethyl alcohol from Acetylene.

19. (a) Answer the following : 1½

(i) Which of the following compounds is the strongest acid ?

$$HC\equiv CH,\ CH_3CH_2OH,\ CH_3COOC_2H_5,\ CH_3CHO$$

(ii) Which of the following is the strongest base ?

$$HC\equiv C^{\ominus},\ CH_3CH_2^{\ominus},\ CH_2=CH^{\ominus}$$

(iii) Which of the following is the strongest electrolyte ?

CH_3CONH_2, $C_6H_5NO_2$, $C_6H_5NH_2$, $C_6H_5N\_Cl$

(b) Which reagent would you use for the conversion of benzal chloride to benzaldehyde—$Ca(OH)_2$ or NaOH ? Give reasons. 1½

20. Name the reagents and state the conditions in the following reaction : 1+1+1

(i) Benzene to Acetophenone, (ii) Deamination of Aniline, (iii) Dehydration of Acetamide.

21. In minor cuts during shaving we use common alum to stop bleeding. What is its reason ? 1

22. Benzene is a planar molecule. Is tolune also planar ? Give reason. 1

23. An organic compound on reaction with water produces methanol and hydrogen peroxide. Write the structure of the compound. 1

24. Why is platinum wire employed in the flame test ? 1

25. It is not safe to distil diethyl ether kept in laboratory for a long time. Why ? 1

26. What is power alcohol ? 1

27. Which one of the following ion would give a basic solution upon addition to water ?

(a) NH_4^+, (b) Na^+, (c) CH_3COO^-, (d) NO_3^-.

28. Which of the following has the least effect on the solubility of a solid in water ? 1

(a) Nature of solute, (b) Temperature, (c) Pressure.

29. The half-lives of radioactive $^{235}_{92}U$ and $^{238}_{92}U$ are 0.71×10^9 and 4.51×10^9 years respectively. Which one of them has the faster rate of decay ? 1

30. Of the following fuels, which one produces the lowest concentration of pollutants under normal condition ? 1

(a) Coal, (b) Wood, (c) Natural gas, (d) Petroleum.

H.S. CHEMISTRY : 1994

First Paper

Group – A

(Answer any *FOUR* questions)

1. (a) State the law of reciprocal proportion and illustrate it with an example.

(b) How the law of reciprocal proportion can be deducted and explained by Dalton's atomic theory ?

(c) Ammonia contains 17·65% hydrogen, water contains 11·11% hydrogen and nitrous oxide contains 36·36% oxygen. Show how these data illustrate the law of reciprocal proportion. 3 + 4 + 3

2. (a) At 25°C, the vapour density of gas is 25. What will be its vapour density at 50°C ?

(b) How many hydrogen and oxygen atoms are present in a spherical drop of water of radius 1 mm at 4°C ?

(c) How can the relation $PV=nRT$ be utilised to determine the molecular weight of a gas ? Find out the dimension of R.

(d) What is the difference between 'density' and 'vapour density' of a gas ? 1 + 4 + 3 + 2

3. (a) Establish a relation between 'equivalent weight' and 'atomic weight' of an element.

(b) 10 gm of an element A combines with 25 gm of another element B. The equivalent weight of A being 20, find the equivalent weight of the element B.

(c) Explain why the hydrogen displacement method is not suitable for determining the equivalent weight of sodium.

(d) How is it ascertained whether crystals of two compounds are isomorphous or not ? Name two compounds with dissimilar formulas but having isomorphous crystals. 2 + 2 + 3 + 3

4. (a) Give one example each of 'peroxide' and 'basic salt'.

(b) What are the acidity of MgO and basicity of H_3PO_3 ?

(c) Which indicator would you use for the titration of sodium carbonate solution with sulphuric acid ? What would be the change of colour at the end point ?

(d) When would the normality of a solution be same as its molarity ? Give an example.

(e) Why is the strength of Sodium chloride solution expressed in terms of formality instead of molarity ?

(f) In what proportion by volume $0{\cdot}2(N)$ sodium hydroxide and $0{\cdot}3(N)$ sodium hydroxide solutions are to be mixed to obtain a $0{\cdot}24(N)$ solution of sodium hydroxide ?

(g) There are two bottles, one containing 100 ml $0{\cdot}1(N)$ HCl and the other 100 ml $0{\cdot}1(N)$ H_2SO_4. State with reasons whether the number of hydrogen ions in the two will be different.

1 + 1 + 2 + 2 + 2 + 1 + 1

5. (a) Why is chemical equilibrium termed 'dynamic equilibrium' ?

(b) Write down the relation between K_p and K_c for the reaction :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(c) What is the effect of (i) change of pressure, and (ii) continuous removal of ammonia from the reaction mixture in the reaction .

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(d) The solubility of ammonia in water at constant temperature and pressure is decreased in the presence of sodium hydroxide in solution—how can you explain this phenomenon in the light of chemical equilibrium concept ? 2 + 1 + 4 + 3

6. (a) State Faraday's laws of electrolysis.

(b) Show that $E = Z.F.$, where E=Chemical equivalent, Z=Electrochemical equivalent of and element and F=Faraday.

(c) How many grams of sodium are deposited at the cathode by one Faraday of electricity ?

(d) Calculate the volume of electrolytic gas (at NTP) liberated when 10 amp current is passed through acidified water for 100 secs.

[1 Faraday = 96,500 coulomb]

(e) What is the total charge in coulomb carried by Avogadro number of electrons ?

3 + 2 + 1 + 3 + 1

Group – B

(Answer any *FOUR* questions)

7. How do you prepare ? (any *four*)
   (a) Hydrogen bromide from bromine.
   (b) Hydrogen sulphide from sodium sulphate.
   (c) Orthophosphoric acid from calcium phosphate.
   (d) Carbon from carbon monoxide.
   (e) Boron from boric acid. $4 \times 2^1/_2$

8. (a) How can you remove
   (i) bromine gas from a mixture of bromine and hydrogen bromide gases.
   (ii) nitric oxide from a mixture of nitric oxide and nitrous oxide.

(b) Give a chemical test to distinguish between dilute hydrogen peroxide solution and an aqueous solution of ozone.

(c) How can you prove that
   (i) White phosphorus and red phosphorus are allotropes of the same element ;
   (ii) phosphine is less basic than ammonia.

(d) Which one is purer—distilled water or deionised water ? Give reasons.

(1 + 1) + 2 + 4 + 2

9. (a) Describe how pure chlorine gas be prepared chemically at room temperature.

(b) What conclusions can you draw about the salts used from the following observations ?
   (i) A salt on strong heating gives off brown fumes.
   (ii) A white salt on strong heating gives off colourless, odourless gas and the residue turns yellow when hot but white when cold.

(iii) When silver nitrate solution is added to an aqueous solution of a salt, a curdy white precipitate is formed, which readily dissolves in ammonium hydroxide.

(iv) The salt solution turns transiently violet when sodium nitroprusside solution is added to it.

(c) How is anhydrous hydrofluoric acid prepared ? 4 + 4 + 2

10. Explain with reasons : (any *four*)

(a) Fluorine gas cannot be prepared electrolytically from liquid hydrogen fluoride or hydrofluoric acid solution.

(b) Orthoboric acid is a weak monobasic acid but in the presence of glycerol its aqueous solution behaves like a stronger acid.

(c) Nitrous acid can act as both oxidising and reducing agents.

(d) Permanent hard water cannot be softened by boiling alone.

(e) Nitrous oxide is not prepared in the laboratory by heating ammonium nitrate alone.

4 × 2½

11. Write with equations what happens when : (any *four*)

(a) Phosphine gas is passed through an aqueous solution of silver nitrate.

(b) Ammonia reacts with chlorine.

(c) A filter paper strip moistened with potassium iodide and starch solution is held in chlorine gas.

(d) Calcium carbide is heated in presence of nitrogen at 1100°C and the product formed is hydrolysed.

(e) Carbon is heated with conc. sulphuric acid. 4 × 2½

12. (a) Write down the physico-chemical principle involved in the synthesis of sulphuric acid by the contact process.

(b) What is oleum ?

(c) How is ammonium sulphate prepared from gypsum ?

(d) How will you prove the presence of sulphur in sulphuric acid ?

(e) Give an example of conc. Sulphuric acid being used as a dehydrating agent .

4 + 1 + 2 + 2 + 1

JT. ENT. CHEMISTRY : 1994

Attempt all questions.

1. (a) Write a short account on "isotopy" and "allotropy" of hydrogen. 2½+1½+1=5

(b) With balanced chemical equation write one chemical reaction where hydrogen can be obtained by the action of sodium hydroxide on a metal.

2. (a) Write down electronic configuration of

(i) Ca and (ii) Ne. 2+1½+1½=5

(b) Mention the "Groups" of Mendeliev's Periodic table in which the following elements have been placed—(i) Al, (ii) P and (iii) Br.

(c) What do you mean by "one mole of electron" ?

3. (a) Two metals (M_1 and M_2) have the same equivalent weight, but the atomic mass of M_1 is twice the atomic mass of M_2. How can you explain this ? 1

(b) 4.00 gram of a powder known to contain only copper, zinc and aluminium were treated with excess of warm dilute hydrochloric acid until reaction was complete. The undissolved material after filtration, washing and drying weighed 1.50 gram. The filtered solution and washings were treated with ammonium chloride solution and ammonium hydroxide in slight excess. A colourless precipitate was produced. After filtration, washing, drying and ignition to constant weight, it left a product weighing 2.55 gram. Calculate the percentage composition of original powder. (Al=27, O=16). 4

4. (a) A gas is collected partially in an eudiometer tube over water at room temperature. This is wet gas. How would you find out the pressure of the dry gas collected ? State the law you would use for the purpose. 2

(b) The atomic weight of a metal is 50.9 and it forms a chloride of unknown composition. Electrolysis of the molten chloride produces 1.0 gram of metal for every 2.8 gram of Cl_2 (gas). Find the empirical formula of the chloride. 3

5. (a) Why was it necessary to consider the existence of neutrons in the nucleus of an atom ? 2

(b) How was neutron discovered ? Give the reaction. 1

(c) Name the terms you could use to represent the relationship between (i) A and D and (ii) B and C in the following radioactive transformation. 2

$$A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C \xrightarrow{-\beta} D$$

Give reason for your answer.

6. (a) Find the number of covalent bonds in $C_2H_4O_2$. 1

(b) How can you explain the formation of (i) NH_4^+ from NH_3 and (ii) BH_4^- from BH_3. 2

(c) (i) Which bond has greater ionic character : H-F or H-Cl ? Give reason. ½

(ii) The boiling point of NH_3 is greater than that of HCl. How can you account for this ? 1½

7. (a) If solid iodine is heated in an open test tube it sublimes, but if it is heated slowly in a sealed test-tube it melts to a liquid. How can you explain this ? 1½

(b) What is the difference between a deliquescent substance and a hygroscopic substance ? Explain with one example each. 1½

8. What is meant by : 1+1+1=3

(a) Physical atomic weight ; (b) Chemical atomic weight ; (c) Atomic mass unit (a.m.u.).

9. Write down chemical names and molecular formula of the following compounds : 1+1+1+1+1=5

(i) Borax, (ii) Green vitriol, (iii) Phosgene, (iv) Carborundum, (v) Epsom salt.

10. (a) $KClO_3$ is taken in a hard glass test-tube (A) and a mixture of $KClO_3$ and MnO_2 (4:1) is taken in another similar hard glass test-tube (B). The two hard glass test-tubes are placed side by side in a sand bath and both are heated.

(i) From which tube liberation of gas will start first ? ½

After the evaluation of gas has ceased, water is added into the hard glass tube and the mixture is filtered after shaking it thoroughly.

(ii) What is present in the filtrate ? ½

(iii) What is the residue and what is its role in the preparation of above gas. 1

(iv) How is the gas used in the melting and welding of metal sheets. ½

(v) When a colourless gas is mixed with this gas a brown gas is produced. What is the colourless gas ? ½

(vi) Will a vacuum be created if an iron wire or coal tar are burnt in a sealed bottle containing the above gas ? 1

(b) How can you get NH_3 from $NaNO_2$? 1

11. (a) (i) Two samples of water contain the same cations Ca^{2+} and Mg^{2+}, but one is marked as temporary hard water and the other as permanent hard water. In which respect do they differ ? 1

(ii) A sample of water contains 0.012 gram of $MgSO_4$ per litre of water. Express the hardness of this sample of water in ppm. [C=12, O=16, Mg=24, S=32, Ca=40] 1½

(b) (i) Which acid is more advantageous for the preparation of hydrogen peroxide from barium peroxide—dilute H_2SO_4 or syrupy phosphoric acid ? Give reasons for your answer. 1

(ii) How many grams of H_2O_2 is present in 10 ml of "10 volume H_2O_2" ? 1½

12. State what happens when :

(i) Hydrochloric acid is added to an aqueous solution containing potassium bromide and potassium bromate. 1

(ii) A mixture of boric acid and calcium fluoride is treated with concentrated sulphuric acid. 1

(iii) An aqueous solution of potassium iodate acidified with dilute sulphuric acid is treated with white phosphorous. 1

(iv) Ferric oxide is fused with sodium carbonate. 1

(v) 1-2 drops of cobalt nitrate solution is added to aluminium oxide taken in a charcoal groove and the mixture is heated by an oxidising blowpipe flame. 1

13. (a) Write down the stepwise reactions that are involved in the manufacture of sodium carbonate by the Solvey process. Why is potassium carbonate not prepared by this process ? 2+1=3

(b) What happens when the hydrate, $MgCl_2$, $6H_2O$ is heated ? How do you obtain anhydrous magnesium chloride ? 2

14. (a) In a qualitative analysis of metallic radicals in Gr. II on passing H_2S a black precipitate is obtained which may be either CuS or PbS. How would you confirm that it is CuS and not PbS ? Answer with equation. 2

(b) (i) Cite one chemical characteristic in which HF differs from other hydrogen halides. 1

(ii) How can you remove HF from a mixture containing F_2 and little HF ? 1

15. (a) Give reasons for the following : 3

(i) In the preparation of hydrogen iodide from alkali iodides, phosphoric acid is preferred to sulphuric acid.

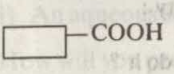
(ii) Bleaching of flowers by Cl_2 is permanent while by SO_2 it is temporary.

(iii) Precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in presence of HCl and not HNO_3.

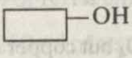
(b) Arrange the hydrogen halides in the increasing order of 1

(i) dipole moment ; (ii) reducing power.

16. Here is a list of formulae for some carbon compounds. The rectangles represent carbon chains (which are not necessarily the same).



(i)



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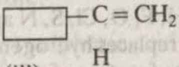

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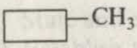

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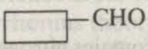


(v)

(a) Which two compounds would react together under suitable conditions to form an oily ester ? Give the formula of the ester produced. Name a suitable catalyst for the reaction. 1½

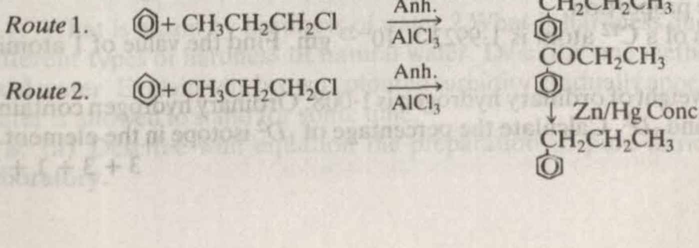
(b) Which two compounds would react together under suitable conditions to form an acetal ? Give the formula of the acetal produced. Name a suitable catalyst for the reaction. 1½

(c) Which two compounds could be decomposed by heat to form an alkene ? ½

(d) Which compound could react by addition polymerisation to form a plastic ? ½

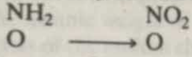
(e) Which compound would react with hydroxylamine hydrochloride in the presence of sodium acetate to form an oxime ? What is the role of sodium acetate in the reaction ? ½+½=1

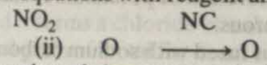
17. (a) Below are given two different routes for the preparation of 3-phenylpropane :



Which route would you prefer for the actual preparation of 3-phenylpropane ? Give reasons. 1

(b) How would you convert (give arrow head equations with reagent and conditions).

(i) 
$C_6H_5NH_2 \longrightarrow C_6H_5NO_2$

(ii) 
$C_6H_5NO_2 \longrightarrow C_6H_5NC$ 1+1=2

(c) Give arrow head equations for the preparation of phenol from a hydrocarbon in which propanone is obtained as a by-product. 2

18. (a) A solid organic compound C_6H_8NCl in its aqueous solution reacts acidic to litmus. On adding $NaNO_2$ solution and then alkaline β-napthol gives scarlet red precipitate. Identify the compounds and explain the reactions.

(b) How you will introduce $-CH_3$ and CH_3CO—group in benzene nucleus ? 3+2=5

19. (a) What are the major products in the following reactions ? 1

$$(CH_3)_3C\cdot CHO + HCHO \xrightarrow[NaOH]{50\%\ aqueous}$$

(b) How would you separate ethanol and propanone from a mixture containing the two ? 1

(c) How would you distinguish between $CH_3CH_2C \equiv CH$ and $CH_3CH_2CH = CH_2$? 1

20. Describe, with relevant equations, the laboratory method of preparation of chloroform. What happens when chloroform is warmed with a few drops of aniline and alcoholic KOH ? 3

21. Which of the following are isotones ? 1

$${}^{226}_{88}Ra,\quad {}^{227}_{89}Ac,\quad {}^{228}_{88}Ra,\quad {}^{228}_{89}Ac,\quad {}^{234}_{90}Th$$

22. In many spray-bottles from which a perfume is sprayed contain a very harmful substance. By what name it is commonly known ? Why is it harmful ? 1

23. In which group of the Periodic table solid, liquid and gaseous—all three types of elements are found ? What are these elements ? 1

24. Pure aniline is colourless, but when kept exposed in air it becomes coloured. Why ? How can you obtain colourless aniline from it ? 1

25. Arrange in order of decreasing or increasing electronegetivity : 1
H, F, O, Cl, S, N and C

26. Why zinc replaces hydrogen from H_2SO_4 but copper cannot do it ? 1

27. What is the function of "Cryolite" in the extraction of metal. Name the metal also. 1

28. State why hard water is softened before use in boilers. 1

29. What is the Thermit process ? 1

30. How would you prove that ammonia contains nitrogen ? 1

H.S. CHEMISTRY : 1995

First Paper

Group – A

(Answer any *FOUR* questions)

1. (a) State the law of multiple proportion and explain it with an example.

(b) Two elements *A* and *B* combine with each other and form two compounds containing 88·88% and 94·12% of *B*. Show that these data are in agreement with the law of multiple proportion.

(c) The mass of a C^{12} atom is $1{\cdot}9923 \times 10^{-23}$ gm. Find the value of 1 atomic mass unit in gm.

(d) Atomic weight of ordinary hydrogen is 1·008. Ordinary hydrogen contains two isotopes, ${}_1H^1$ and ${}_1D^2$. Calculate the percentage of ${}_1D^2$ isotope in the element.

3 + 3 + 1 + 3

2. (a) State Avogadro's hypothesis and show that the molar volume of a gas is 22·4 litres at NTP.

(b) A Gas mixture contains 80% N_2 and 20% O_2 by volume. Calculate the average vapour density of the gas mixture.

(c) Define : (i) gram molecular weight

(ii) formula weight.

(d) Equal number of hydrogen and oxygen atoms are present in a compound composed of these two elements. If its molecular weight is 34, what should be its molecular formula ? 4 + 3 + 2 + 1

3. (a) What is meant by the equivalent weight of an element ?

(b) 1 gm of a metal, *M* forms 3·9165 gms of the metal chloride. Find the equivalent weight of the metal.

(c) 'Chile saltpetre contains small quantities of sodium iodate.'—Explain.

(d) What is meant by partial pressure of a gas ? State Dalton's law of partial pressure. Establish the relation among partial pressure, mole fraction and total pressure of the gas mixture.

(e) 'Ordinary rubber balloons, filled with hydrogen gas, are often found to contract after some time.'—Why ? 1 + 2 + 1 + 5 + 1

4. (a) Explain :

(i) Na_2HPO_3 is a normal salt.

(ii) 20 ml of a $(\frac{N}{20})$ Na_2CO_3 solution requires 20 ml of a $(\frac{N}{20})$ HCl solution for neutralisation when titrated using methyl orange as the indicator, but 10 ml of the same HCl solution is required when the same titration is carried out using phenolphthalein as indicator.

(iii) An aqueous solution of ferric chloride is acidic.

(b) How will you prepare 250 ml of a standard $(\frac{N}{10})$ sulphuric acid solution ?

$(2^1/_2 \times 3) + 2^1/_2$

5. (a) State and explain Arrhenius theory of electrolytic dissociation.

(b) Establish the relation among the charge of an electron (*e*), Avogadro's number (*N*) and Faraday (*F*).

(c) A current of 0·50 amp, when passed through a solution of $CuSO_4$ for 1 hour, liberates 0·59 gm of Cu. Find the equivalent weight of Cu. (*F*=96,500 coulomb). 4 + 3 + 3

6. (a) State and explain the law of mass action.

(b) Discuss using Le Chatelier's principle the effects of change in temperature and pressure on the reaction :

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O + 216 \text{ K. Cal}$$ 4 + 6

GROUP—B

(Answer any *FOUR* questions)

7. What is meant by hardness of water ? What is hardness due to ? Explain the different types of hardness of natural water. Describe one method of softening of hard water. Explain why brown coloured turbidity gradually appears when tubewell water is allowed to stand for some time. 1 + 2 + 2 + 3 + 2

8. (a) Describe with equation the preparation of pure nitric oxide gas in the laboratory.

(b) What happens when sodium nitrate solution is added to an aqueous solution of ferrous sulphate acidified with sulphuric acid ? Give equations.

(c) Give the name of an oxide that forms two oxyacids in aqueous solution.

(d) What is "fuming nitric acid" ? 4 + 4 + 1 + 1

9. (a) Describe briefly the preparation of pure carbon monoxide from oxalic acid.

(b) Describe with equation the preparation of hydrogen peroxide. What is meant by "10 volume" hydrogen peroxide ? Explain with equation the reaction of hydrogen peroxide with ozone. 3 + (3 + 2 + 2)

10. State with equations what happens when : (any *four*)
   (a) Powdered borax is heated,
   (b) Phosphorus trichloride is boiled with water,
   (c) A mixture of conc. nitric acid and phosphorus is heated,
   (d) Potassium iodide is added to a solution of copper sulphate,
   (e) Sodium nitrite is boiled with zinc dust and strong solution of caustic soda.

$2\frac{1}{2} \times 4$

11. (a) Compare and contrast among the halogen elements with reference to oxidising power, reactions with water and acidity of hydracids.

(b) Why does a freshly prepared colourless solution of hydroiodic acid turn brown on keeping ?

(c) Illustrate with examples to show that sulphur dioxide can act both as an oxidant as well as a reductant. 6 + 2 + 2

12. (a) Discuss the physico-chemical principle involved in the Haber's process of manufacture of ammonia gas.

(b) Show with an experiment that ammonia is highly soluble in water and its aqueous solution is alkaline.

(c) How will you detect ammonia in the laboratory ? 6 + 3 + 1

JT.ENT. CHEMISTRY : 1995

Attempt ALL *questions.*

1. (a) State Le Chatelier Principle. 1

(b) Below is given a reversible reaction at a fixed temperature :

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + 22\text{ K Cal} :$$

   (i) Write the equation for k_p of the above reaction.
   (ii) What is the relation between k_c and k_p for the above reaction ? ½
   (iii) What will be the effect on the point of equilibrium of the reaction if the pressure of the system is increased at equilibrium at fixed temperature ? Will the numerical value of k_p change under this condition ? 1½

(c) The reaction between zinc sulphate solution and hydrogen sulphide is reversible. The equation for the reaction is :

$$\underset{\text{Colourless}}{Zn^{2+}(aq)} + \underset{\text{Colourless}}{H_2S(aq)} \rightleftharpoons \underset{\text{White}}{ZnS(s)} + 2H^+(aq)$$

What substance (other than one of the reactants and products) could you add to the mixture at equilibrium to make more zinc sulphide ? 1

2. Name the element predicted by Mendeleev as ekaboron and indicate its position in the periodic table. Arrange the elements of the third period in the order of increasing atomic number. Explain why the electronegativity increases along a period from left to right but decreases down a group when atomic number increases in both cases. Justify, mentioning two points, the inclusion of Ca and Mg in the same group of the periodic table. 1 + 1 + 2 + 1

3. (a) "Water is an amphiprotic solvent". Explain with chemical equations the "acid-base" character of water. 2

(b) H_2O and H_2S are hydrides of elements of the same group of periodic table but one is liquid and the other is gas at room temperature. Explain. $1\frac{1}{2}$

(c) To an aqueous solution of borax phenolphthalein is added and then glycerol. Write observations and inference. $1\frac{1}{2}$

4. (a) An element (take the symbol as M) has 26 protons in the nucleus of its atom. Write the electronic configurations of M^{2+} and M^{3+}. $\frac{1}{2} + \frac{1}{2}$

(b) (i) Will $^{235}_{92}U$ and $^{238}_{92}U$ show the same radioactivity ? Answer with reason. 1

(ii) Of the following three isotopes of Pb, which one is the end number of the radioactive series starting with $^{232}_{90}Th$? 1

$^{210}_{82}Pb$, $^{208}_{82}Pb$ and $^{206}_{82}Pb$.

(c) (i) Find out the oxidation number of sulphur in $S_2O_8^{2-}$. $\frac{1}{2}$

(ii) Write balanced equation for the reaction between copper (II) sulphate and phosphine. Show from the consideration of oxidation number whether the reaction is a redox reaction or not. $1\frac{1}{2}$

5. (a) Calculate the molarity of a solution that contains 1·22 g of haemoglobin (MW 68300) in 165 ml of solution. 2

(b) What volume of gas will be produced at 523 k and 1 atmosphere pressure by the explosive decomposition of 5 gram of ammonium nitrate according to the following equation ?

$2NH_4NO_3 (S) = 2N_2 (g) + O_2 (g) + 4H_2O (g)$. [H = 1, N = 14, O = 16] 3

6. (a) Define oxidation in terms of oxidation number and state its value for Mn in $KMnO_4$. If M be the molecular weight of $KMnO_4$, what would be its equivalent weight in its reaction with ferrous sulphate in acid medium ? 2

(b) The following metals are arranged from top to bottom in the electropotential series : K, Ca, Mg, Zn, Cu, Ag. Predict (i) whether K or Mg will displace hydrogen gas from cold water more violently, (ii) whether K or Cu will act as more powerful reducing agent and (iii) whether Zn will displace Ag from a solution of Ag^+ or Ag will displace Zn from a solution of Zn^{++}. 3

7. (a) A bucket of turbid river water does not become clear even on standing for a long time. Why ? How can you make this turbid water clear ? Explain. $1\frac{1}{2}$

(b) A patient with kidney failure is kept on dialysis. What is meant by dialysis ? What is the purpose of dialysis for the patient with kidney failure ? Explain. $1\frac{1}{2}$

8. (a) The atomic numbers of two elements A and B are 9 and 17 respectively.

(i) The atom of which element (between A and B) is smaller in size ?

(ii) Which has lesser electronegativity ?

(iii) Which has greater oxidising property ?

Answer with reason. 2

(b) What information can be obtained about a molecule from the fact that its dipole moment is zero ? Answer with two different examples. 1

9. (a) How is galena (PbS) present as impurity removed from the ore zinc blende ? 1

(b) In which of the following cases flux is required ?

(i) In the smelting of roasted zinc blende.

(ii) In the extraction of iron from haematite in the blast furnace.

Explain. Mention the name of the flux with the purpose it serves where it is required. 2

(c) What is 'anode mud' in connection with the metallurgy of copper ? What is its importance ? 2

10. (a) How is anhydrous hydrogen fluoride prepared ? 2

(b) A precipitate is produced when a gas mixture containing PH_3, P_2H_4 and H_2 is passed through a HI-filled gas jar.

(i) Write the name and formula of the precipitate.

(ii) What reaction occurs between the precipitate and KOH solution ?

1 + 1

(c) How can you explain that CO is combustible in air, but CO_2 is not ? 1

11. (a) How can you prepare hydrogen peroxide from sulphuric acid ? 2

(b) Give examples of

(i) reducing property of H_3PO_3.

(ii) peroxidising property of hydrogen peroxide.

(iii) acidic property of ferric oxide. 1 × 3

12. (a) State, with equations, what happens when hydrogen peroxide is treated with alkaline potassium ferricyanide solution. 1 × 5

(b) White phosphorus reacts with cold copper sulphate solution.

(c) Metallic zinc reacts with cold and very dilute nitric acid.

(d) Ammonia is passed through a suspension of gypsum in water and then carbon di-oxide is passed through the liquid.

(e) A mixture of calcium phosphate, coke and silica is heated in an electric furnace.

13. Write, with equation, what happens when :

(a) Sodium sulphate is heated strongly with carbon and the residue is made to react with an aqueous solution of zinc sulphate.

(b) Sodium aluminate solution is heated with ammonium chloride.

(c) An aqueous solution of potassium iodide in which chloroform has been added is shaken gradually with chlorine water in excess.

(d) A mixed solution of sodium nitrate and caustic soda is heated with aluminium powder.

(e) Fluorine reacts with cold dilute solution of caustic soda. 1 × 5

14. Give a flow diagram for the Haber process for the synthesis of ammonia. 4

15. (a) What may be the cause of high boiling point of sulphuric acid ? How chemists put the high boiling of sulphuric acid to practical use ? Give one example. 2

(b) Will there be any problem if the amount of CO_2 in atmospheric air, (i) greatly increases, (ii) greatly decreases ? Explain. 2

16. (a) An organic compound (A) having the molecular formula C_4H_9Cl on reaction with hot caustic potash solution produces two isomeric alkenes (B) and

(C). On ozonolysis of the mixture of (B) and (C) the following three compounds are obtained :

(i) HCHO, (ii) CH_3CHO and (iii) CH_3CH_2CHO.

Find out the structures of (A), (B) and (C).

(b) Two different organic compounds (X) and (Y) when separately treated with iodine and caustic soda produce the same compounds—sodium ethanoate and iodoform.

(i) What are (X) and (Y) ? 1

(ii) How can you convert (X) to (Y) and vice versa ? 1

17. (a) How can you convert—

(i) methane to acetylene ;

(ii) sodium formate to sodium oxalate ;

(iii) aniline to benzene ? 1 + 1 + 1

(b) (i) Urea and acetamide are separately treated with $NaNO_2$ and dil. HCl. Write the products in each case.

(ii) Formaldehyde is treated with ammonia. Give the product with structure. $1\frac{1}{2} + \frac{1}{2}$

18. (a) How can you distinguish—

(i) Formaldehyde and acetaldehyde ;

(ii) Methyl alcohol and ethyl alcohol ;

(iii) Benzyl chloride and chloro benzene ? 1 + 1 + 1

(b) Explain and exemplify—

(i) Haloform reaction ;

(ii) Cannizzaro reaction. 1 + 1

19. (a) Below are given one route (ROUTE 1) for the preparation of propane and one route (ROUTE 2) for the preparation of methoxyethane :

ROUTE 1

$$CH_3CH_2Br + CH_3Br \xrightarrow[\text{Ether}]{\text{Na}} CH_3CH_2CH_3 + NaBr$$

ROUTE 2

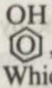
$$CH_3CH_2I + CH_3ONa \xrightarrow{\text{Heat}} CH_3CH_2OCH_3 + NaI$$

ROUTE 2 is a good method for the preparation of methoxyethane but ROUTE 1 is not a good method for the preparation of propane.—Why ? $1\frac{1}{2}$

(b) How can you prepare ethylbenzene by using ethyne as the only organic substance and any material of your choice. $1\frac{1}{2}$

20. (a) How can you detect the presence of nitro group in nitrobenzene without using any acid ? 1

(b) Arrange the following compounds in order of increasing acidity : 1



, $H-C\equiv C-H$, H_2CO_3, CH_3CH_2OH

(c) Which of the following compounds will react with NaOH ?

CH_3COCH_3, $CH_3CH(OH)CH_3$, CH_3CH_2CHO, CBr_3COCH_3 1

21. Unlike metals, crystals of ionic compounds do not conduct electricity—Why ? 1

22. Why aluminium chloride forms a dimer ? 1

23. Two moles of sodium nitrate and one mole of potassium sulphate are dissolved in 1 litre of water. What other two salts may be used to prepare the same solution ? 1

24. Write the structure of an organic compound containing seven hydrogen atoms which produces a white precipitate when conc. HCl is added to it, but the precipitate dissolves on shaking with water. How does this happen? 1

25. Why ethanol, sodium dichromate and sulphuric acid are not mixed together initially and then distilled in the preparation of acetaldehyde? 1

26. How many neutrons are there in 5×10^{-4} mole of ^{14}C? 1

27. What is meant by 10 volume H_2O_2? 1

28. A trihydric alcohol is used in domestic purpose. Write structural formula. 1

29. Sulphur di-oxide gas is passed through acidified potassium permanganate solution. Write balanced chemical equation. 1

30. FeS_2 is burnt is oxygen. Show the products with balanced chemical equation by oxidation-reduction method. 1

H. S. CHEMISTRY : 1996

FIRST PAPER

GROUP—A

Answer any *four* questions

1. (a) State the law of constant proportions.

(b) Establish the law from Dalton's atomic theory.

(c) SO_3 contains 40% by weight of sulphur, H_2S contains 94.11% by weight of sulphur and water contains 11.11% by weight of hydrogen. Prove that these data are in accordance with law of reciprocal proportions. 2+4+4

2. (a) Prove that molecular weight of a gas is twice its vapour density.

(b) A gaseous hydrocarbon contains 75% by weight of carbon. 100 cc of the gas at NTP weighs 0.0720 gm. Determine the molecular formula of the hydrocarbon. [1 litre of Hydrogen gas at NTP weighs 0.09 gm.]

(c) Molecular weight of a gas is 80. What will be the volume of 0.2 gm of the gas at 23°C and 740 mm pressure? 3+4+3

3. (a) Describe briefly the determination of equivalent weight of zinc by hydrogen displacement method.

(b) A solution contains 0.1 gm-equivalents of NaOH. How many gm-moles of NaOH are present in the solution?

(c) State Dulong - Petits law. What are its limitations? How can the atomic weight of an element be determined by using this law?

(d) The acid, H_3PO_3, has molecular weight 82. Its equivalent weight is 41. What is the basicity of the acid? 4+1+(1+1+2)+1

4. (a) Explain why :—

(i) An aqueous solution of ammonium acetate is neutral though the salt suffers hydrolysis.

(ii) BaO_2 is called a peroxide.

(iii) The solution obtained by adding 40 gms of solid sodium hydroxide to 1000 cc distilled water is not 1(N).

(b) 25 cc of a 0.14 (N) HCl solution is required to react completely with 0.1902 gm of an impure sample of lime stone. Find out the percentage of $CaCO_3$ in the sample.

(2 × 3)+4

5. (a) State Boyles law for gases.

(b) Draw graphs to show variation of volume and P.V product of a gas against pressure at constant temperature. The gas is assumed to obey Boyles law.

(c) Prove that the rate of diffusion of any gas is inversely proportional to the square root of its molecular weight.

(d) 224 cc of nitrogen and 112 cc of oxygen gas, both at NTP, were mixed and kept in a vessel at 27°C and 2 atmospheric pressure. What is the volume of the vessel?

2+2+2+4

6. (a) What is solubility curve? Mention any two informations obtained from such curve.

(b) What is supersaturated solution?

(c) Define electrode & electrolyte. What happens when a solution of copper sulphate is electrolysed between two copper electrodes.

(d) Write down the units of : (*any four*)

(i) Current (ii) electrochemical equivalent. (iii) equivalent weight (iv) solubility of a solute in a solvent (v) Universal gas constant. (2+1)+1+(2+2)+2

GROUP—B

Answer any *four* questions.

7. (a) Describe briefly the manufacture of hydrogen peroxide by electrolysis of sulphuric acid solution. Give equations.

(b) Why is anhydrous Barium peroxide is not used in the laboratory preparation of hydrogen peroxide?

(c) How would you obtain pure ozone from ozonized oxygen?

(d) Why is lather not formed from soap in hard water? 4+2+2+2

8. (a) Prove that both graphite & lamp black are allotropic modifications of the same element.

(b) Explain why diamond is so hard.

(c) How can pure carbon monoxide be obtained from an impure sample of carbon monoxide?

(d) Why can dilute sulphuric acid not be used in preparation of CO_2 from $CaCO_3$? Give equations.

(e) CO_2 cannot be used as fire extinguisher when temperature is very high—explain.

2 × 5

9. (a) How can you confirm the presence of boric acid in a sample? Give equations.

(b) What is nitrolim? How is it obtained? How does it work as a fertilizer?

(c) What is aqua regia? Why is it called so?

(d) Discuss the use of hydrogen sulphide gas as a reagent in qualitative inorganic analysis. 2+3+2+3

10. State with equations what happens when :—(*any four*)

(a) Carbon dioxide is passed through brine saturated with ammonia.

(b) Hydrogen peroxide reacts with solution of $K_2Cr_2O_7$.

(c) Ammonia gas reacts with excess chlorine.

(d) Sulphur dioxide gas is passed through a solution of potassium permanganate.

(e) Phosphine gas is passed through an acidified solution of copper sulphate slowly.

(f) Potassium iodide is added to a solution of copper sulphate acidified with acetic acid.

$2\frac{1}{2} \times 4$

11. How would you prepare (Only condition, equation & separation of product to be given) :—*Any four*

(a) Ammonium sulphate from gypsum.

(b) Boron from boron trioxide.

(c) Nitrogen gas from sodium nitrite.

(d) Ammonia from sodamide.

(e) Phosphine from phosphorus.

(f) Chlorine gas from hydrogen chloride. $2\frac{1}{2} \times 4$

12. (a) Discuss the physico-chemical principles involved in the manufacture of nitric acid from oxidation of ammonia by Ostwald process.

(b) How can you convert sulphuric acid to sulphurous acid.

(c) Concentrated sulphuric acid is added to a concentrated hydrochlone acid solution. The evolved gas on reaction with ammonia gas yield a white solid. Identify the evolved gas and the solid. 6+2+2

JT. ENT. CHEMISTRY : 1996

Attempt ALL *Questions*

1. (a) What are the essential differences between the phenomena of "Osmosis" and "Diffusion" as applied to a solution? State one practical use of each. 1+1

(b) Calculate the molarity of 1 litre of pure water at 4°C. Will this molarity change if the sample of water is cooled to 0°C or heated to 100°C? Will your conclusions be same for molality? 1+1+1

2. (a) How can you distinguish between a true solution and a colloidal solution by a simple physical process in the laboratory? Mention an industrial application of the physical property of a colloidal system made use of in the above physical process. 1+1

(b) The radioactivity of 1 gm. of a radioactive radium sample is 1 curie. What amount of radioactivity will be shown by the radium sulphate salt obtained by reacting this sample of radium completely with 20 ml. of $3NH_2SO_4$? Explain your result. $1\frac{1}{2}$

(c) The dipole-moment value of HF molecule is 2.00 D. The HF bond distance is 0.92 A°. Calculate the percentage ionic character of HF bond. $1\frac{1}{2}$

3. (a) A solid element burns in oxygen without a change in volume (of gaseous substances) under the same conditions of temperature and pressure. If the gaseous product has a density of 32, what is the element and what is its equivalent weight? 2

(b) What is the nature of the graph if logarithm of pressure of an ideal gas is plotted against logarithm of its volume at definite temperature? Will the nature of plot change if logarithm of (PV) product of an ideal gas is plotted against pressure of the gas at constant temperature? 1+1

(c) Why Mohr's salt is a double salt but not potassium ferrocyanide? 1

4. (a) State Gay Lussac's law. 1

(b) Two oxides of an element A contains 27.5 and 30.0 percent oxygen respectively. The formula of the second one is A_2O_3. Calculate the formula of the first one. 2

(c) State the law of constant proportion. Point out exception, if any. Is the converse statement of the law always true? Your answer must be supported by examples. 2

5. (a) Using Faraday's laws how can you calculate the value of the charge on a Cu^{+2} ion in the appropriate units? What is the value of this charge? $1\frac{1}{2} + \frac{1}{2}$

(b) One gram of a radioactive material with a half-life period of 2 years is stored for six years. How much of the material remains intact? $1\frac{1}{2}$

(c) 8.25 gm. of a saturated solution of sodium carbonate at 27°C, required 138 ml. of 0.25 N hydrochloric acid for complete neutralisation. Calculate the solubility of sodium carbonate at 27°C. $1\frac{1}{2}$

6. (a) Haemoglobin was found to contain 0.335% iron (At wt of Fe = 56). The molecular wt of Haemoglobin is 1.67×10^4. Find the number of Fe atoms in the Haemoglobin. 2

(b) When 0.75 mole solid A_4 and 2 mole gaseous O_2 heated in a sealed vessel (bomb), completely mixing up the reactants and producing only one compound (gaseous), it is found that when the temperature is reduced to the initial temperature, the contents of the vessel exhibit a pressure equal to half the original pressure. Find the formula of the compound formed explaining the observation. 3

7. State how the following informations are symbolised in a chemical reaction like $A + B \rightarrow C + D$:

(a) Exothermic nature of the reaction; $\frac{1}{2}$

(b) Endothermic nature of the reaction; $\frac{1}{2}$

(c) A compound is formed as precipitate; $\frac{1}{2}$

(d) One of the reactants is in aqueous solution form; $\frac{1}{2}$

(e) A gaseous product is formed; $\frac{1}{2}$

(f) A reversible reaction. $\frac{1}{2}$

8. (a) Find (i) the total number of neutrons, and (ii) the total mass of neutrons in 7 mg. of ^{14}C. [Assume the mass of a neutron to be equal to the mass of a hydrogen atom.] 2

(b) What is the product formed by the decay of ^{14}C, which is a β-emitter? To which group of the periodic table does the product belong? $\frac{1}{2} + \frac{1}{2}$

9. Write, giving equations, what happens when : 1 × 5

(a) A paste of bleaching powder is heated with a few drops of cobalt chloride solution.

(b) Ozone is passed into an aqueous solution of potassium iodide and the resulting solution is tested with litmus.

(c) SO_2 gas is passed into a suspension of MnO_2 in cold water.

(d) Aqueous solution of ferric sulphate and potassium iodide are mixed.

(e) Ferric oxide is fused with sodium carbonate and the product treated with hot water.

10. A green amorphous powder (A) when heated gives off a colourless gas (B) which turns lime-water milky and the black-residue (C). (C) dissolves in dilute HCl and the resulting solution gives a chocolate precipitate on adding potassium ferrocyanide solution. (A) dissolves in HCl with the evolution of a gas which is identical in all respects with (B). The solution of (A) as obtained above gives a black precipitate (D) on passing H_2S. Another portion of this solution gives a precipitate (E) with NaOH solution and the precipitate remains unaffected on further addition of the base. Identify the compounds (A) to (E). 5

11. (a) Write an equation to illustrate each of the following metal extraction principles : 1 × 3

(i) Self reduction process,
(ii) thermit process,
(iii) carbon reduction process.

(b) In the carbon reduction process of extracting magnesium, state the temperature at which the reduction is carried and add a note on the process of collection of the metal and formation of metallic slabs. 2

12. (a) Explain the following : 1 × 3

(i) Aluminium cannot be extracted from purified bauxite by carbon reduction process.

(ii) Sodium can be extracted from fused NaCl by electrolysis but not from fused $NaNO_3$.

(iii) A basic flux is used in the extraction of iron whereas in the extraction of copper an acidic flux is used.

(b) What is the real reducing agent of haematic in the blast furnace? What is tempering? What is its utility? $\frac{1}{2} + 1 + \frac{1}{2}$

13. (a) State the electrodes, electrode reactions and conditions for

(i) extraction of Na from fused NaCl by electrolysis; 2
(ii) preparation of NaOH from NaCl solution by electrolysis. 2

(b) When solution of Zn^{+2} was added to a solution of NaOH, a clear solution was obtained. When NH_4Cl was added to the clear solution, $Zn(OH)_2$ precipitated. Explain these observations using chemical equations. 1

14. How can you carry out the following preparations? (give reagents, reaction conditions and arrowhead conversions only): 1 × 4

(i) Sulphur di-oxide at room temperature,
(ii) Carbon monoxide from marble,
(iii) Minium from litharge,
(iv) Ammonium sulfate without using sulfuric acid.

15. (a) What changes are observed when cobalt nitrate solution is added to alumina heated to a high temperature? 1

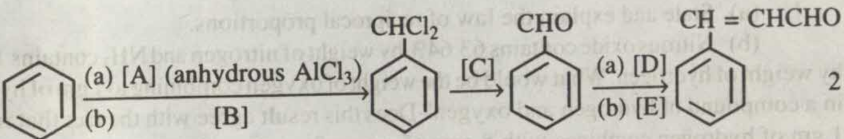
(b) Why the wooden shelf under the reagent bottle containing concentrated H_2SO_4 blackens after some time? 1

(c) How will you distinguish between borax and boric acid by a single chemical test? 1

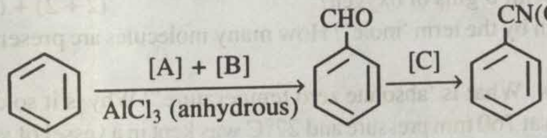
(d) 'Iron pyrities is not directly smelted in the blast furnace to produce pig iron'—Why? 1

16. Identify the compounds marked [A], [B], [C], [D] etc. in the following sequence of reactions :

(a) $CH_3COOH \xrightarrow{[A]} CH_3COCl \xrightarrow{[B]} CH_3COCHN_2 \xrightarrow[Ag_2O\ catalyst]{[C]} CH_3CH_2COOH.$ 1½

(b) 

2

(c) 

1½

17. State what happens :
(a) when acetamide is treated with caustic soda in presence of bromine; 1
(b) when chlorine gas is passed through boiling toluene; 1
(c) when glacial acetic acid is heated with PCl_3; 1
(d) glacial acetic acid is treated with acetylene gas in presence of $HgSO_4$ and the resultant product is distilled; 1
(e) phenol is treated with zinc dust. 1

18. How will you carry out the following conversions?
(a) Carbon di-sulfide into chloroform; 1½
(b) Quick lime into benzene; 1½
(c) Benzene into phenyl acetic acid. 2

19. What happens in the following cases when : 1 × 3
(a) acetone is heated with hydrazine followed by sodium ethoxide;
(b) toluene is treated with chromyl chloride and the product is hydrolysed;
(c) benzaldehyde is heated with acetic anhydride in presence of sodium acetate at 180°C.

20. How will you distinguish between the following pairs of compounds by chemical method? 1 × 3
(a) Benzyl chloride and chlorotoluene;
(b) Acetone and ethyl alcohol;
(c) Methyl amine and methyl ethyl amine.

21. What is the role of limestone in the extraction of iron? 1

22. Arrange in the descending order of carbon contents : 1
stainless steel, mild steel, cast iron and wrought iron.

23. Explain why $(NH_4)_2SO_4$ solution is acidic. 1

24. Name the catalyst used in the contact process of manufacturing H_2SO_4. 1

25. Which of the following has the highest boiling point? 1
H_2, He, Ne, Xe, CH_4.

26. Does the H^+ ion concentration of pure water change with temperature (increase, decrease or unchanged?) 1

27. What is the percentage of silver in "German silver"? 1

28. Name a non-metal which can liberate hydrogen from an alkali. 1

29. 'Petrol fire cannot be extinguished by spraying water'—Why? 1

30. Which of the following compounds is used in the preservation of biological specimens?
(i) CH_3CHO, (ii) CH_3COOH, (iii) CH_3-O-CH_3, (iv) HCHO.

H. S. CHEMISTRY : 1997

First Paper

Group—A

Answer any *four* questions

1. (a) State and explain the law of reciprocal proportions.

(b) Nitrous oxide contains 63.64% by weight of nitrogen and NH_3 contains 17.65% by weight of hydrogen. What would be the weight of oxygen combining to 1 gm of hydrogen in a compound of hydrogen and oxygen? Does this result agree with the fact that in water 1 gm of hydrogen combines with 8 gms of oxygen? (2 + 2) + (4 + 2)

2. (a) What do you mean by the term 'mole'? How many molecules are present in 14 gms of nitrogen?

(b) State Charles' law. What is 'absolute zero temperature'? Why is it so called?

(c) 16 gms of oxygen at 760 mm pressure and 27°C was kept in a vessel of volume 12.30 litres. The entire gas was transferred into a vessel of 24.60 litres of volume at the same pressure. Find the temperature of the gas in the larger vessel. (1 + 2) + (2 + 1 + 1)+ 3

3. (a) State with suitable examples Arrhenius concept of acids and bases.

(b) Deduce the relationship between electrochemical equivalent and chemical equivalent.

(c) A solution of cupric chioride was electolysed between two copper electrodes for 35 minutes using a current of 0.56 ampere. How much copper would be deposited at the cathode?

[Electrochemical equivalent of Cu = 3.28×10^{-4} gm/coulomb] 6 + 2 +2

4. (a) What do you mean by a 'chemical equilibrium'? Why is it called a dynamic equilibrium?

(b) State Le-Chatelier's principle. Discuss the effect of changes in temperature and pressure on the equilibrium :

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + 24 \text{ K. Cal.}$$

(Here *g* stands for gaseous state.)

Deduce the relationship between K_p and K_c for this equilibrium.

(2 + 1) + (2 + 1 + 1) + 3

5. (a) Define the terms normality and molarity. Find the molarity of 1 normal solution of each of hydrochloric acid, sulphuric acid and phosphoric acid.

(b) Aqueous solution of NaCl is neutral, but aqueous solution of Na_2CO_3 is alkaline,—Explain.

(c) 20 gms of a metal on reaction with dilute sulphuric acid liberates 0.504 gm of hydrogen. How much metallic oxide will be produced from 2 gms of the metal?

(1 + 1 + 1 + 1 + 1) + 2 + 3

6. (a) Explain the term 'water of crystallisation'. 1.26 gms of a hydrated crystalline compound of molecular weight 126 leaves 0.90 gm of residue on dehydration. Find the number of water of crystallisation per molecule of the compound.

(b) Establish the relation $F/_N = e$, the terms have their usual meanings.

(c) 0.93 gm of a compound consisting of C, H and N on complete combustion produces 2.64 gms of CO_2 and 0.63 gm of water. In a separate experiment 0.186 gm of the same compound yields 24.62 c.c. of nitrogen at 1 atmospheric pressure and 27°C. Molecular weight of the compound is 93. Find its molecular formula. (1 + 2) + 3 + 4

Group—B

Answer any *four* questions

7. (a) Describe a laboratory method of preparation of pure and dry ammonia.

(b) Describe an experiment to show that ammonia is highly soluble in water and its aqueous solution is alkaline. 6 + 4

8. (a) Explain why fluorine cannot be obtained by electrolysing either an aqueous solution of hydrogenfluoride or of liquid hydrogen fluoride. How would you prepare fluorine in the laboratory?

(b) Compare the reactions of F_2 and Cl_2 with aqueous of solution NaOH. Give equations. (3 + 3) + 4

9. (a) What do you mean by 'hardness of water'? What are hardness due to? Describe the ion-exchange method of softening of hard water. Give equations.

(b) Calculate the percentage strength of "100 volume" hydrogen peroxide. (2 + 2 + 4) + 2

10. (a) Discuss the physico-chemical principles involved in the large scale production of sulphuric acid by contact process.

(b) Give one example in each case where sulphuric acid acts as an oxidant and as a dehydrating agent. Give equations. 6 + (2 + 2)

11. State with equations what happens when : 5 × 2

(i) Carbondioxide gas is passed through limewater initially in small amount and finally in large excess.

(ii) Carbonmonoxide gas is passed into ammoniacal solution of cuprous chloride.

(iii) Phosphine gas is passed through an aqueous solution of silver nitrate.

(iv) H_2S gas is passed through an acidified solution of potassium dichromate.

(v) Nitrogen gas is passed over heated calcium carbide and the product is hydrolysed.

12. How would you prepare the following? State the conditions and give equations : 3 + 3 + 2 + 2

(i) Ozone from oxygen,

(ii) Boric acid from borax,

(iii) Urea from ammonia,

(iv) Hydrogen gas from water gas.

JT. ENT. CHEMISTRY : 1997

1. (a) Write the ideal gas equation and state why the gas constant in this equation is called universal gas constant. What is the difference between real gas and ideal gas? $^1/_2 + 1 + ^1/_2$

(b) Show graphically the relationship between volume and temperature at constant pressure and from there explain the concept of absolute zero. 1 + 1

(c) Calculate the value of the universal gas constant in Litre-atmosphere. 1

2. (a) Find the unit of $(^{RT}/_{F})$ where, F, is Faraday. 1

(b) A metal wire carries a current of 1 ampere. How many electrons pass a point in the wire in 1 sec? 2

(c) Current of 2.00 amp. passing for 5 hr. through a molten tin salt deposits 22.2 gm tin. What is the oxidation state of the tin in the salt? [At. wt. of tin = 118.7] 2

3. (a) Atomic number is a better standard of periodicity than Atomic weight—Justify. 1

(b) Why the electron affinity of fluorine is lesser than that of chlorine? 1

(c) What is "Lanthanide Contraction"? 1

(d) Which one is more alkaline, MgO or Al_2O_3? Why? 1

(e) Why is the ionisation potential of Be more than that of B? 1

4. (a) State Dulong and Petit law of heat capacity of solids. 1

(b) Two 10 gms of bars of two metals (at. wt. = A_1 and at. wt. = A_2) are heated to 60°C and then immersed in identical, insulated containers each containing 200 gms of water at 20°C. Which metal will cause a greater temperature rise in the water? (Given: $A_1 > A_2$) 2

(c) Arrange the solubility of AgCl in decreasing order in the following solutions: 1
H_2O, 0.1 N $AgNO_3$, 0.1 N KCl, 0.1 N $CaCl_2$.

(d) For which of the following species, Bohr's theory does not apply? 1
(i) H (ii) H^+ (iii) He^+ (iv) Li^{+2}

5. Name the process by which you would separate :

(a) Ammonium Chloride from its mixture with NaCl. 1

(b) Sodium Chloride from its mixture with Sodium Sulfate. 1

(c) Calcium Fluoride from its mixture with Calcium Chloride. 1

(d) 10 c.c. of $^{N}/_{10}$ Na_2CO_3 solution is titrated with $^{N}/_{10}$ HCl solution from a burette using : (i) Methyl Orange as indicator. (ii)Phenolphthalein as indicator. Will the two burette readings be same? If not, why not? Explain your answer. 2

6. (a) 4.08 gm of mixture of BaO and an unknown carbonate MCO_3 was heated strongly. The residue weighed 3.64 gm. This was dissolved in 100 ml of 1 N HCl. The excess of acid required 16 ml of 2.5 N NaOH for complete neutralisation. Identify the metal M. 4

(b) Arrange the following in order of increasing H^+ ion concentration: 1
0.1 N NaCl, 0.1 N NH_4Cl, 0.1 N NH_4CH_3COO, 0.1 N $NaCH_3COO$.

7. (a) Give the set of quantum numbers that describe an electron in a 3p orbital. 1

(b) Give the electronic configuration of Ni and Ni^{+2} (At. No. of Ni = 28). Find the number of unpaired electron in each case. 2

8. State with reason whether the two reactions noted below are oxidation-reduction reactions or not:

$$NaCl + AgNO_3 = AgCl + NaNO_3; \quad 2H_2S + SO_2 = 3S + 2H_2O$$

Which one is the oxidising agent and which one the reducing agent? Name the oxidised and reduced products. 2 + 1

9. (a) State what happens when air and steam are passed alternatively over a bed of red hot carbon. State one industrial application of this reaction. 2

(b) CO_2 gas is passed through ammoniacal brine solution at 35°C. State one industrial application of the reaction. $1^{1}/_{2}$

(c) Ferrous sulphate crystals are heated in presence of air. State one industrial application of the reaction. $1\frac{1}{2}$

10. (a) How would you prepare 'pure' bauxite for electrolysis purpose from crude bauxite? 2

(b) How would you prepare $AlCl_3$ from Al_2O_3? Give equation. 1

(c) State the commercial preparation of 'bleaching powder'. What is 'available chlorine' of a sample of bleaching powder? 2

11. (a) B is a gas with a distinctive smell. It is neutral and turns starch-potassium iodide paper blue. When B is heated and then cooled back to room temperature, the volume is found to have increased by 50% (measured at the same pressure). Identify the gas. 2

(b) Classify the following elements having atomic numbers as given below into three separate pairs on the basis of similar chemical properties: 9, 12, 16, 34, 53, 56. 3

12. (a) Why aluminium is not extracted by çarbon reduction of alumina? (b) What is the function of fluospar in elctrolysis of alumina? (c) What happens if the content of alumina in the electrolytic bath falls below a certain percentage? (d) What is sodium ferrite? (e) What is 'Calorising'? 1 × 5

13. Name the metals present in:

(a) Bronze, (b) Stainless Steel, (c) Monel metal, (d) Calamine, (d) Duralumin. 1 × 5

14. (a) What do you understand by 20 volume H_2O_2? Calculate the percentage composition of this H_2O_2. $2\frac{1}{2}$

(b) Calculate the hardness of a water sample in ppm which contains 0.01 gm $MgCl_2$ per litre. $1\frac{1}{2}$

15. (a) How would you remove

(i) nitric oxide from a mixture of nitric oxide and nitrogen? 1

(ii) ammonia from a mixture of ammonia and oxygen? 1

(b) Suggest tests which could be used to distinguish among NO, N_2O_5 and NO_2 2

16. (a) Label the secondary hydrogen(s) in 2-Methylbutane. 1

(b) Which of the isomeric butyl alcohols give positive iodoform test? Write the structure only. 1

(c) Which of the following compounds will give effervescence with $NaHCO_3$?

Phenol; Benzoic acid; Aniline; Aniline hydrochloride.

(d) Ozonolysis of compound A($C_{10}H_{18}$) yields two equivalents of acetone and one equivalent of OHC-CH_2-CH_2-CHO. Give the structure of A. 1

(e) Adipic acid ($C_6H_xO_y$) is a homologue of oxalic acid $\left(\begin{array}{c}\text{COOH}\\ | \\ \text{COOH}\end{array}\right)$. Find X and Y. 1

17. Mention one test to distinguish between (give equation):

(a) Nitro benzene and Aniline; (b) Benzene and Phenol; (c) Acetaldehyde and Acetone; (d) Methyl alcohol and Ethyl alcohol; (e) Methane and Ethylene.

18. How will you prepare? (give equations only): 1 × 5

(a) Polyethylene from ethanol; (b) A primary amine from an amide; (c) Ethylene oxide from ethylene; (d) p-dinitrobenzene from p-nitroacetanilide; (e) p-xylene from toluene.

19. Write the structure of 3-bromo-2-butanol. Which carbon atoms in the molecule are linked to four different ligands (atoms or groups)? Specify the ligands in each case. 1+2

20. (a) State the Marconikof's rule. Give an example. 1

(b) What is polymerisation reaction? Give an example. 1

21. Correct the following statement—Neutralised solution of an acid does not contain any H^+ or $(OH)^-$ ion. 1

22. Calculate the weights in gram of one fluorine atom [F-19, H-1] 1

23. Na^+ is more stable than Na.—Explain.

24. How can you prove that aniline is basic in character? 1

25. Name a metal which may be extracted from the respective one by both electrolytic and carbon reduction process. 1

26. How will you obtain D.D.T. from benzene? [Give equations only.] 1

27. Which of the following are covalent? NaH, Cl_2O, K_2O, H_2. 1

28. If three-fourth quantity of a radioelement disintegrates in two hours, find its half-life. 1

29. Write the structure of a four carbon containing organic compound which dissolves in conc. H_2SO_4, but reappears on dilution with water. 1

30. Name the constituents of the following alloys and mention one important use of each : (a) Duralumin; (b) Aluminium Bronze.

H. S. CHEMISTRY : 1998

First Paper

Group—A

Answer any *Four* questions

1. (a) Establish the law of multiple proportions from Dalton's atomic theory. 4

(b) 30 gms of a compound 'D' on analysis gives 10 gms of an element 'A' and 20 gms of an element 'B'. 45 gms of another compound 'E' gives 15 gms of 'B' and 30 gms of an element 'C'.

15 gms of 'A', 60 gms of 'B' and 15 gms of 'C' are mixed together and reacted. What would be the amount of 'D' and 'E' produced? What would be the weight of the mixture after reaction? It is to be assumed that only reaction possible is between 'B' and 'A' or 'C'. Mention which of the laws of chemical combination are used here. 4+2

2. (a) Prove that at N.T.P. the volume of 1 mole of any gas is 22.4 litres. 3

(b) Draw PV-P and P-$^1/_v$ curves for an ideal gas at constant temperature & explain their nature. 3

(c) Measured at the same temperature and pressure 2 vol. of ozone on dissociation give 3 volumes of oxygen. 40 ml. of a mixture of ozone and oxygen on being heated and then being brought under the same conditions of temperature and pressure gives a measurement of new volume to be 42 ml. Calculate the percentage of volume of ozone in the gas mixture. 4

3. (a) State Mitscherlisch law of isomorphism. Explain with an example. Mention two exceptions to the law. 2+1+1

(b) Find out the equivalent weights of $FeCl_2$ and $KMnO_4$ in the reaction.

$$KMnO_4 + 5FeCl_2 + 8HCl = KCl + MnCl_2 + 5FeCl_3 + 4H_2O$$

[Given that Molecular weight of $KMnO_4 = 158$, Molecular weight of $FeCl_2 = 126.85$] 2

(c) What are the changes that take place when a Copper sulphate solution is electrolysed between Copper electrodes? 2

(d) What will be the concentrations of K^+ and Cl^- in a mixture of 50 cc 0.2 (N) KCl and 25 cc 0.1 (N) NaCl? 2

4. (a) State and explain the law of mass action. 2+1

(b) Explain the effect of addition of inert gas on a chemical equilibrium. 2

(c) Discuss the effect of catalyst on chemical equilibrium. Why is a catalyst used at all during a chemical process? 2+1

(d) Explain with the help of Le-Chatelier's principle why the concentration of sulphide ion drops upon addition of hydrogen chloride to a solution of hydrogen sulphide. 2

5. (a) Express in molarity the concentration of hydrogen ion as is generated in a 0.4 (N) H_2SO_4 solution. 1½

(b) What is an indicator? Cite an example. 1½

(c) 0.8775 gms of a salt is dissolved in water and made upto 100 ml. Express the strength of the solution in normality. (Equivalent weight of the salt = 58.5) 3

(d) To 25 ml. of a solution of NaOH are added 10 ml. of 0.7 (N) H_2SO_4 solution and to this alkaline solution are added 10 ml. of 0.5 N HCl solution to make it fully neutralised. Calculate the strength of the NaOH solution is normality and gms/litre. (Na = 23) 4

6. (a) What is solubility curve? What are its main uses? 1+2

(b) Put forward an explanation for the abnormal solubility curve of sodium sulphate. 2

(c) Write short notes on :

(i) Dialysis and its use. 3

(ii) Use of alum as coagulant. 2

Group—B

Answer any *Four* questions

7. (a) Describe the preparation of pure hydrogen peroxide in the laboratory. (Mention the reagents required, condition for the reaction, chemical equation & purification) 4

(b) What is 'trailing of mercury'? 2

(c) Prove that ozone is a stronger oxidizing agent than hydrogen peroxide. 2

(d) 100 gms of a sample of hard water contains 0.00475 gms of Magnesium chloride. Find out the hardness of the water.

(Mg = 24, Cl = 35.5, Ca = 40) 2

8. (a) Prove that white phosphorus and red phosphorus are allotropic modifications of the same element. 2

(b) Cite an example for reducing action of iodine with equation. 2

(c) Prove that hydrogen sulphide contains sulphur. 2

(d) Write down the reaction for preparation of chlorine gas at room temperature. 2

(e) How would you convert rhombic sulphur to monoclinic sulphur. 2

9. (a) Give examples of additive compounds made by NO and CO. 1+1

(b) Explain why dil H_2SO_4 cannot be used for the preparation of CO_2 from $CaCO_3$ but can be used if it is prepared from $NaHCO_3$. 2

(c) NH_3 and CO_2 is passed through suspension of Gypsum in water. What is the product? 2

(d) What are Coal gas and Nitrolim? Mention their uses. 2+2

10. (a) 'Zinc and copper react differently with concentrated hydrochloric acid but in a similar way with concentrated nitric acid'—explain. 3

(b) 'Nitrous acid has got oxidizing as also reducing property'—explain. 2

(c) How would you separate nitric oxide and nitrous oxide from a mixture of two? 2

(d) How is boric acid distinguished from a borate salt? 2

(e) 'Hydrogen fluoride is a liquid but hydrogen chloride is a gas'—explain. 1

11. State with equations what happens when :—(Attempt any ***Four***)

(a) Bone ash is heated with concentrated sulphuric acid.

(b) Dry ammonia gas is passed over hot sodium metal and the solid product is reacted with water.

(c) Colemenite is boiled with sodium carbonate solution.

(d) Boric acid is heated up to 140°C.

(e) Sodium nitrate is heated with Zinc metal and sodium hydroxide solution.

(f) Hydrogen sulphide gas is passed through acidified potassium dichromate solution. $4\times2^1/_2 = 10$

12. (a) Discuss the physico chemical principle involved in the manufacture of nitric acid by Ostwald process. 4

(b) Show that Nascent Hydrogen is more reducing than ordinary Hydrogen. 2

(c)(i) In a saturated solution of 'A' HCl gas is passed. The solid 'A' separates out; (ii) When $AgNO_3$ solution is added to a solution of 'A' a curdy white precipitate 'B' is obtained. (iii) B is soluble in ammonia solution but insoluble in nitric acid.

Identify 'A' and 'B'. Explain the processes (i), (ii) and (iii). 1+3

JT. ENT. CHEMISTRY : 1998

1. (a) (i) Which elements are called transitional elements?

(ii) Can Cu (atomic number 29) and Zn (atomic number 30) be called transitional elements? Explain. 1+2

(b) Name one property which is not a periodic property of the elements. 1

(c) Calculate the atomic volume of sodium (atomic mass = 23). The density of sodium is 0.972 g/ml. 1

2. (a) Below are given atomic mumber of five elements :

(i) 12, (ii) 17, (iii) 18, (iv) 19, (v) 21.

With which of the above elements an element of atomic number 20 has the greatest tendency to combine chemically? Explain mentioning the nature of the bond. 3

(b) A nucleide, ${}^{A}_{Z}X$, emits successively *m* numbers of α-particles and *n* numbers of β-particles. Write the symbol of the end nucleide (${}^{?}_{?}Y$).

(c) Complete the following equation.

$${}^{9}_{4}Be + ? = {}^{12}_{6}C + ?$$

3. (a) In which of the following least number of molecules are present?

(i) 1.12 litre of SO_2 at S.T.P., (ii) 1 g mol of SO_2, (iii) 32 g of SO_2, (iv) 4×10^{23} molecules of SO_2. Explain. 2

(b) (i) A sample of hydrogen gas occupies a volume of 69.37 cm^3 at a pressure of exactly 1 atm when immersed in a mixture of ice and water. When the gas (at the same pressure) is immersed in boiling benzene, its volume expands to 89.71 cm^3. What is the boiling point of benzene?

(ii) In the above example the temperature has not been measured by using mercury. How then is the temperature measured here? 2+1

4. (a) On which of the following depends the choice of indicator in an acid-alkali titration?

(i) Only acid, (ii) only alkali, (iii) both acid and alkali, (iv) none of these. Explain. 2

(b) What volume of 98% sulphuric acid (specific gravity 1.84) is required to prepare 1 litre of 2M, sulphuric acid? [H = 1, O = 16, S = 32] 3

5. (a) When a hydrogen bond is symbolised by X—H ——Y, what do the solid and dotted lines represent? Which distance is shorter? 1

(b) Write a plausible Lewis structure for the chlorite ion ClO_2^-. Show the formal charges on each atom, and the net charge. 1

(c) Identify red-ox reaction(s) and the reducing and oxidising agent(s) from the following reactions.

(i) $2MnO_4^- + 5SO_2 + 6H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H_3O^+$

(ii) $NH_4^+ + PO_4^{3-} \rightarrow NH_3 + HPO_4^{2-}$

(iii) $HClO + H_2S \rightarrow H_3O^+ + Cl^- + S$ 3

6. (a) Thomas Graham observed that cane sugar and urea could readily pass through animal membranes from their aqueous solutions, but glue and gelatin could not pass through animal membranes from their aqueous solutions. How can the phenomena be explained? 2

(b) To a saturated aqueous solution of potassium iodide crystals of KI^{131} are added. Will the aqueous solution become radioactive? Explain. [I^{131} is radioactive.] 1

(c) For the following reaction

$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$

will the value of equilibrium constant remain unchanged, if the reaction occurs in (i) a closed vessel, (ii) an open vessel, at unchanged temperature? Explain. 2

7. (a) Find the number of electrons in a drop of sulphuric acid weighing 4.9×10^{-3} mg. [Assume it to be cent percent pure.] 1

(b) Cite an exception to the law of multiple proportion. 1

(c) State that postulate of Bohr's theory with which the kinetic energy of the electron in an atom of hydrogen or any similar particle can be calculated. 1

8. (a) The first ionization energy of elements generally increases with atomic numbers of the elements in a period of the periodic table. Why? Cite an exception. $1\frac{1}{2}$

(b) Boron (atomic weight 11) from a gaseous hydride of atomicity 8; on analysis, 2.8 g of the hydride was found to contain 0.6 g of hydrogen. Find the formula of the hydride. $1\frac{1}{2}$

9. (a) A sample of water collected from a pond is found to contain 12.0 ppm concentration of CO_3^{2-}. Calculate the molarity of CO_3^{2-} in this water sample [Atomic weight of C = 12, O = 16] 1

(b) An air sample is found to contain 7.0 micrograms per m^3 of carbon monoxide. Calculate the concentration of carbon monoxide in ppm at NTP. 2

(c) How H_2O_2 can be stored in laboratories without appreciable decomposition? 2

10. (a) Write the balanced chemical equation when iodine reacts with sodium thiosulfate in almost neutral medium. Hence, calculate the equivalent weight of sodium thiosulfate if its molecular weight be M. 1+1

(b) Explain the following facts :

(i) In the iodometric estimation of Cu^{2+}, NH_4SCN is added. $1^1/_2$

(ii) Cl_2-water is kept in laboratories in dark bottles. $1^1/_2$

11. (a) How you can detect $CO_3{}^{2-}$ and $SO_3{}^{2-}$ each in a mixture of the two? $1^1/_2$

(b) Though C and O differ much in electronegativity, the molecule carbon monoxide has a near-zero dipole moment. Explain. 2

(c) Which one between H_3PO_3 and H_3PO_4 is more acidic? Explain. $1^1/_2$

12. (a) State with balance chemical equation what happens when K metal is burnt in SO_2. 1

(b) SO_2 and SO_3 pollution in air is a global problem now-a-days, particularly in urban and industrial areas. Mention two major sources of SO_2 and SO_3 in air and discuss their damaging effects with particular reference to acid rain. 1+3

13. Solid mixture of A and B when warmed with conc. H_2SO_4, a deep red gas (vapour) C is evolved which is soluble in dil. caustic soda solution to produce yellow coloured solution D. D on acidification with dil. acetic acid and then on reacting with lead acetate solution produces yellow solid E, which is soluble in dil. HNO_3. On acidification aqueous solution of A changes colour. Both A and B make the flame golden yellow in the usual flame test for basic radicals. Identify A to E with all the chemical reactions involved. Detailed balancing of equations are not necessary but write all the reactants and products in all the reactions. 5

14. (a) Calcium reacts with air, but the metal obtained during its extraction by electrolysis of fused calcium chloride does not do so—explain why. 1

(b) how would you convert sulphur quantitatively to hydrogen sulphide? 1

(c) 'Rusting is an electrolytic phenomenon'—explain. 1

(d) Give a method for estimation of carbon monoxide in air. 1

15. (a) Name the compounds formed by combination of two or more of the elements K, C, O, H, S and Cl which would show the following characteristics :

(i) Compound is diatomic, electrovalent and conducts electricity in fused state.

(ii) Compound is triatomic gas, soluble in water to some extent and used as an analytical agent.

(iii) Compound is diatomic gas, soluble in water and solution strongly acidic.

(iv) Compound is diatomic gas, almost insoluble in water and highly poisonous. 2

(b) A sample of water of hardness 200 ppm contains calcium chloride and calcium bicarbonate. One litre of it is boiled when 0.102 g $CaCO_3$ is precipitated. Calculate permanent hardness. 1

(c) Write down the equation for the reaction that takes place when potassium ferricyanide is heated with sulphuric acid. 1

16. (a) An alkane has a molecular weight of 72 and monochlorination produces one product only. Give IUPAC name of the compound. Give reasons for your answer. 1

(b) What are the following?

(i) Fehling's solution, (ii) Tollen's reagent, (iii) Bayer's reagent, (iv) Brady's reagent. 2

(c) Two alkyl iodides RI and R'I are mixed and subjected to Wurtz reaction. Butane, pentane and hexane are the products. Give graphical formulae of RI and R'I. 1

(d) (A) $\xrightarrow[Hg^{2+},\ 80^\circ C]{20\%\ H_2SO_4}$ (B) $\xrightarrow{I_2/\text{alkali}}$ $CHI_3 + CH_3COO^-$. What are (A) and (B)? 1

17. (a) C_2H_5NO represents two isomeric compounds, both of which can be prepared from acetylene. One of these compounds gives off a pungent smelling gas on boiling with caustic soda solution. What are the compounds? Write down the steps of their preparation from acetylene. 3

(b) (i) Name a reagent with which acetaldehyde may be transformed into ethyl acetate in a single step.

(ii) Name the reaction by which phenol may be converted into salicylaldehyde. 1

(c) A polyhydroxy alcohol of molecular weight 168, gives an acetyl derivative having molecular weight 294. How many hydroxyl groups are there in the compound? 1

18. (a) An organic compound of molecular formula $C_4H_8Cl_2$ yields 'A' on hydrolysis. 'A' gives a positive reaction with Schiff's reagent and forms an oxime with hydroxylamme. Oxidation of 'A' gives butanoic acid. Suggest the name of 'A' explaining the reactions involved. 2

(b) An aromatic hydrocarbon (B) reacts with methyl iodide in presence of anhydrous aluminium chloride to produce (C). When Cl_2 is passed through (C) in boiling condition, (D) is produced at the first step. (D) on hydrolysis with $Ca(OH)_2$ furnishes a compound which on oxidation with alkaline $KMnO_4$ followed by acidification gives benzoic acid. Identify (B), (C), (D). Furnish arguments and reactions involved. 2

(c) (i) Name the isomer of vinyl alcohol.

(ii) Write the structure of Westrosol.

19. (a) How can you convert 2-propanol to 1-bromopropane?

(b) In the laboratory the following chemicals are available :

Acetyl chloride ethyl alcohol, ammonium chloride, sodium carbonate, ammonium carbonate, ethyl acetate, glacial acetic acid.

How can you prepare acetamide in the laboratory?

(c) How can you detect the presence of amido group in acetamide?

20. (a) Can the formula C_2H_6O represent two metamers? Explain.

(b) 1-butyne and 2-butyne are separately treated with the following reagents:

(i) Na, liquid ammonia; (ii) H_2 (1 mole), Pd ($BaSO_4$), quinoline; (iii) H_2SO_4, H_2O, $HgSO_4$; (iv) H_2/Pt.

Which reagent (;) will produce the same product in both the cases? Write the structure(s) of the product in such case(s). 2

21. What do you mean by a comproportionation reaction? Give one example. 1

22. What is buckminsterfullerene? 1

23. How many accepted elements are there in the latest Periodic Table? Write the same and symbol of the last element. 1

24. (a) Which amalgam is used in filling teeth? 1/2

(b) What is the percentage content of Cr and Ni on 18-8 stainless steel? 1/2

25. What is 'inorganic benzene'? Write its structure. 1

26. Find the missing items:

$$^{23}_{11}Na + {}^{1}_{0}n \longrightarrow {}^{24}_{11}Na + *.$$

$$\hookrightarrow {}^{24}_{12}Mg + *.$$

27. Polyvinyl chloride [PVC$(C_2H_3Cl)_n$] is a bad pollutant in the sense that on combustion it becomes corrosive to environment and causes choking of humans. Suggest the reaction with equation. 1

28. A solution of bromine in benzene is stable indefinitely, but when an iron nail is put in the solution, bromination of benzene occurs fairly rapidly—explain. 1

29. For the preparation of a saturated aqueous solution of sugar more quickly which is the preferred method?

(i) Addition of sugar cube in water which settles down at the bottom, or

(ii) suspension of a sugar cube in water by means of a string. Why? 1

30. As the contact between the tram pentograph and the conductor breaks, a little brown cloud is formed. Why? 1

H. S. CHEMISTRY : 1999

First Paper

Group – A

Answer any ***four*** questions.

1. (a) Discuss the limitations of Dalton's atomic theory. 2

(b) The average atomic weight of chlorine is 35.46. Using this information, determine the percentage of the two isotopes of chlorine having atomic weights 35 and 37. 3

(c) What is meant by "mole"? Calculate the total charge of one mole electron. (Charge of one electron is 1.6×10^{-19} coulomb) 2+1

(d) How many atoms and molecules are present in one gram oxygen? 2

2. (a) Thermal decomposition of x gm $KClO_3$ gives 760 ml O_2 collected over water at 26°C and 714 mm pressure. Calculate x.

(Given aqueous tension at 26°C = 26 mm, Atomic weight : K = 39, Cl = 35.5 and O = 16). 4

(b) A compound of carbon, hydrogen and chlorine contains 10.04% carbon and 89.12% chlorine. The vapour density of the compound is 59.75. Determine its molecular formula. (Given : Atomic weight : C = 12, Cl = 35.5). 3

(c) Compare the rates of diffusion of Cl_2 and HCl. 2

(d) When a football is pumped, the volume and pressure of the gas inside it increases simultaneously. Does it violate Boyle's Law? 1

3. (a) What is the relation between atomic weight and equivalent weight of an element? 1

(b) There is no unit of equivalent weight. Explain. 1

(c) Is it possible to determine the equivalent weight of copper by hydrogen displacement method? 1

(d) Specific heat of magnesium is 0.262. If magnesium chloride contains 25.5% magnesium, calculate the atomic weight, valency of magnesium and the formula of magnesium chloride. 3

(e) Explain the significance and limitations of a chemical equation. 2+2

4. (a) State and explain the two Laws of Electrolysis of Faraday. 4

(b) How long does one ampere current take to electrolyse 0.9 gm water? (1 faraday = 96,500 coulomb) 2

(c) For a gaseous reaction, derive the mathematical relation between the equilibrium constants K_p and K_c. 4

5. (a) Calculate the equivalent weights of $NaHCO_3$ and H_3PO_3. (Given : Na = 23; C = 12; P = 31) 2

(b) State the nature of the salt, $NaHCO_3$. Explain why an aqueous solution of $NaHCO_3$ is alkaline. 1+3

(c) 4.9 gm H_2SO_4 and 2 gm NaOH are present in 50 ml solution. Is the mixture acidic or alkaline? Calculate the normality and molarity of the resulting acid or alkali. (S = 32) 3

(d) Which indicator is suitable to ascertain the neutralisation of acetic acid by sodium hydroxide? 1

6. (a) What is meant by saturated, unsaturated and supersaturated solution? 3

(b) In a solution 69 gm KNO_3 is dissolved in 50 gm water at 70°C. How much KNO_3 will crystallize out, if the solution is cooled to 20°C? (Solubility of KNO_3 is 138 gm at 70° and 32 gm at 20°C) 1

(c) What is meant by deliquescence? Explain with example. 2

(d) What are the differences between true solution and a colloidal solution? 4

Group – B

Answer any *four* questions.

7. (a) Explain why in the laboratory preparation of H_2 gas, impure Zn granules are used instead of pure Zn and dilute H_2SO_4 instead of concentrated H_2SO_4. $1^1/_2+1^1/_2$

(b) What is occlusion? 1

(c) Why is anhydrous $CaCl_2$ not used to dry ammonia gas? 2

(d) What is meant by temporary and permanent hardness of water? Discuss any one of the methods of removing permanent hardness of water. 2+2

8. (a) Discuss the differences between two crystalline allotropes of carbon. 3

(b) What is active charcoal and what are its uses? 1+1

(c) Explain through which natural processes CO_2 is removed from the atmosphere. 1

(d) Explain how the nitrogen of the atmosphere is transferred to soil. 2

(e) Name one gas, other than O_2, which is incombustible but supports combustion. 1

(f) Give an example of acidic property of H_2O_2. 1

9. (a) Give an example of oxidising property of SO_2. 2

(b) Discuss one method for the identification of H_2S. 2

(c) Discuss how H_2O_2 restores the white colour of blackened oil paintings originally painted by $PbSO_4$. 2

(d) Explain with equations, the principle of etching of glass by HF. 2

(e) Explain how the ingredients of a mixture containing sulphur, sand and iodine are separated. 2

10. (a) Compound '*A*' when heated with slaked lime produces a gas '*B*'. '*B*' on reacting with HCl gas gives back '*A*' in form of white powder. If $AgNO_3$ is added to an aqueous solution of '*A*', a white precipitate is obtained, which is soluble in aqueous solution of '*B*' but is insoluble in HNO_3. Identify '*A*' and '*B*' and explain all the reactions. 4

(b) What is dry ice? 1

(c) Why is bleaching by Cl_2 permanent, but that by SO_2 is temporary? 2

(d) How is H_2 gas, prepared in the laboratory, purified? 3

11. Explain with equation what happens in any *four* of the following cases : $4 \times 2^1/_2$

(a) Aqueous ammonia is added to an aqueous copper sulphate solution.

(b) White phosphorous is heated with caustic soda solution.

(c) Sulphur dioxide gas is passed through acidified potassium dichromate solution.

(d) Chlorine gas is passed over slaked lime at 40°C.

(e) Formic acid is heated with concentrated sulphuric acid.

(f) A copper salt is heated with borax in the oxidising flame.

12. (a) Discuss the principles of the manufacture of sulphuric acid by contact process. 4

(b) How can you prepare— 3×2

(i) urea from ammonia? (ii) HI from I_2? (iii) white phosphorous from bone-ash?

JT. ENT. CHEMISTRY : 1999

1. (a) Give the electronic configuration of $_{24}Cr^{3+}$. Find the number of unpaired electron(s) in the ion. 1+1

(b) Complete the following equations :

(i) $^{7}_{3}Li + ^{1}_{1}H \longrightarrow 2*$; (ii) $^{27}_{13}Al + ^{1}_{1}H \longrightarrow ^{28}_{14}Si + *$; (iii) $^{238}_{92}U \longrightarrow ^{234}_{90}Th + *$ 1½

(c) Arrange the following in increasing order of penetration power :
α-ray, β-ray, X-ray, γ-ray. 1
What is the fundamental difference between X-ray and γ-ray? ½

2. (a) Which periodic group consists of all types of elements viz. solid, liquid and gaseous? Name those elements stating their physical state of aggregation. 2½

(b) Who first showed that atomic volume is a periodic property? What are the positions of (i) alkali metals and (ii) non-metals in the atomic volume curve? 1½

(c) Write down chemical formulae of : (i) Copper (I) arsenide; (ii) Magnesium astatide. 1

3. (a) A transistor material has the specification : one atom of boron per 10^{10} atoms of silicon; find the boron content of 2 kg of such material. [Si = 28.1; B = 10.8] 1½

(b) (i) Find the mass of 4.00×10^{-3} mol of sucrose $C_{12}H_{22}O_{11}$.
(ii) How many carbon atoms are there in that 4.00×10^{-3} mol of sucrose? 1½

(c) A polymeric substance $(C_2F_4)_n$, where n is very large, was prepared by polymerization of C_2F_4 in presence of a sulphur-bearing catalyst. The final product was found to contain 0.012% of S. Find the value of n if the polymeric molecule contains 3 atoms of sulphur. 2

4. (a) There are three chlorotoluenes of dipole moments 1.3 D, 1.9 D and 1.78 D. Assign correct orientation to them. 2

(b) Arrange the following types of actions in order of increasing stability :
Covalent bond, hydrogen bonding, dipole-dipole attraction, van der Waal force. 1

(c) Why have the aldehydes higher boiling point that is anticipated from their molecular weight? What is the phenomenon called? 2

5. (a) Find out the relation between the equilibrium constants of the following two reactions:

(i) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; (ii) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ 1

(b) What would be the effect of halving the pressure by doubling the volume on the following system at 550°C?
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ 1

(c) A 15.0 L vessel containing 5.60 g N_2 is connected by means of a valve to a 5.00 L vessel containing 8.00 g oxygen. After the valve is opened and the gases are allowed to mix, what will be the partial pressure of each gas and the total pressure at 27°C? 2

(d) Determine density of H_2S gas at 27°C and 0.82 atm. pressure. 1

6. (a) Explain why blocks of magnesium are often attached to steel frames of ocean-going ships. 1

(b) You are given little potassium chloride, just few drops of phenolphthalein solution, a strip of blotting paper and a wash bottle with water. How would you identify the terminals of a storage cell? 1

(c) 32 mg of a sample of magnesium having a coating of oxide required 20 ml 0.1 N hydrochloric solution for complete neutralisation of the latter. Find the composition of the sample. 2

(d) Balance by oxidation number method : 1
$P + NaOH + H_2O \rightarrow P_2H_4 + NaH_2PO_2$. 1

7. (a) One volume of a gas (G) is mixed with one volume of hydrogen gas at same temperature and pressure and exploded; one volume of water vapour and one volume of nitrogen gas are obtained. Find the molecular formula of the gas. 2

(b) What is torr? 1

8. (a) Aqueous solution of sodium chloride contains sodium and chloride ions, solid sodium chloride also is an aggregate of these ions. But the former is a conductor of electricity while the latter is not. Explain why. 1½

(b) Covalent bond is directed in space. In which property of such compounds is it reflected? ½

(c) How would you prepare negatively charged ferric hydroxide sol.? 1

9. (a) In dry test for nitrate radical you are advised to *warm* (not to boil) the sample with manganese di-oxide and concentrated sulphuric acid. why? 1

(b) What happens when sulphurous acid is boiled in (i) a closed vessel and (ii) an open vessel? 2

(c) Explain why anhydrous sodium carbonate is a primary standard but sodium carbonate decahydrate is a secondary one. 1

(d) Cite a reaction where alkali is formed from two acidic substances. 1

10. (a) In a laboratory method of preparation of nitrogen, chlorine gas is very slowly passed through concentrated solution of ammonia. What would be the harm (if any) if the reverse process is carried out, i.e. ammonia is passed into solution of chlorine? 1

(b) What happens when anhydrides of boric and phosphoric acids react? Give equation. 1

(c) What happens when hypophosphorous acid is heated (equation is to be given)? What is the reaction termed? Why? 2

(d) How can bauxite be used in fixation of atmospheric nitrogen? 1

11. (a) What is causticising process? Why is it so called? 2

(b) In producing cast iron in blast furnace the aim is to reduce ferric oxide to iron. What, then, is the role of air blast? 1

(c) Explain why pure hydriodic acid stored in a bottle acquires brown colour after some time. 1

(d) What happens when 'lunar caustic' is heated? 1

12. (a) What is 'Mischmetal'? 1

(b) Why mohr's salt, not ferrous sulphate, is used in volumetric analysis? 1

(c) What is 'Nitriding' of steel? 1

(d) What is (i) High speed tool steel, (ii) Bell metal, (iii) Chrome steel, (iv) Ultramarine? 2

13. (a) Give conditions and chemical equations for the preparation of hydrogen peroxide using oxygen and a compound containing no peroxy linkage. 2

(b) Give an example of peroxidising property of hydrogen peroxide. 1

(c) What is the difference between the bleaching actions of SO_2 and Cl_2? 1

(d) A sample of Na_2SO_3 is suspected to be contaminated with Na_2SO_4. How can you detect the presence of Na_2SO_4 in the sample? 1

14. (a) Why lead pipes are not used for carrying very soft water? 1

(b) What are the compositions of :

(i) alnico; (ii) copper matte; (iii) commercial bleaching powder, (iv) electrolyte used in Hall and Heroult process? 2

(c) Why does ferric iodide not exist? 1

15. (a) What is the difference between gypsum and plaster of Paris? How one can be converted to another? 1+1

(b) State what happens when (write equations) :

(i) Sodium hydrogen carbonate is added to an aqueous solution of aluminium sulphate. 1

(ii) An aqueous solution of ammonia is added to mercurous chloride. 1

16. How will you convert (give equations only)?

(a) Aniline into dimethyl aniline. 1

(b) Benzene into acetophenone. 1

(c) An amide into a primary amine with one c-atom less. 1

(d) Acetaldehyde into pentacrythritol. 1

(e) Cyclohexanol into adipic acid. 1

17. How will you obtain (show by arrowhead conversion and mention reagents used)?

(a) Formaldehyde from CO and H_2. 1

(b) Vinyl chloride from acetylene. 1

(c) Butadiene from ethanol. 1

(d) Ethanol from ethylene and sulfuric acid. 1

(e) Picric acid from phenol. 1

18. State what happens when (give arrowhead equations only) :

(a) Toluene is oxidised at 170°C and the product reacted with thionyl chloride. 1

(b) Bromine water is passed through phenol. 1

(c) Formaldehyde is reacted with benzaldehyde in presence of NaOH. 1

(d) Benzene is reacted with acetyl chloride in presence of anhydrous $AlCl_3$. 1

(e) Chloroform is treated with Zn and water. 1

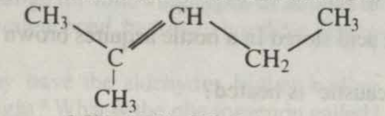
19. (a) In the reaction $Ph\,CH_2MgCl + CH_3CHO \rightarrow PhCH_2CHOHMe + A$, two products are obtained. (A) is an isomer of the alcoholic product and responds to haloform reaction to give an ortho acid of neutralisation equivalent 136. What is (A)? Give reasons for your answer. 2

(b) Give the structure of the simplest compound with empirical formula C_2H. What is its geometrical shape? 1

20. (a) Mark the atoms in the following compounds that lie in a plane: 2

(i) $CH_3CH : CH_2$. (ii) $CH_3CH : CHCH_3$.

(b) Give the dash and condensed structural formula of



21. The name of $CH_3OCH_2CH_3$ is

(a) 2-oxapropane (b) 2-oxabutane (c) 2-oxobutane

Choose the correct name. 1

22. Will a vacuum be created if an iron wire or coal are burnt in a sealed bottle containing oxygen? 1

23. A bottle of acetaldehyde is opened in a summer month in Calcutta. What will be the observation? Why? 1

24. Why lead is included in both Group I and Group II of Group Separation Scheme of inorganic qualitative analysis? 1

25. Name the salt whose composition can be expressed by the molecular formula $H_4O_3N_2$. 1

26. Blood darkens if hydrogen sulphide enters it. Why? 1

27. You are given two aqueous solutions—one of soap and the other of sugar. How can you prove whether the solutions are true solutions or colloids? 1

28. The time required for half disintegration of 0.1 gram of a radioactive isotope is less than that required for the half disintegration of 1 gram of the same isotope. Is the statement true? Give reason. 1

29. How many grams of diamond contain the same number of atoms as 0.1 gram of graphite? 1

30. Indiscriminate use of polythene bags poses a serious environmental pollution hazard. Why? 1

H. S. CHEMISTRY : 2000

First Paper

Group — A

Answer any ***four*** questions.

1. (a) What is meant by 'absolute zero' and 'ideal gas'? 2

(b) Name one unit of the universal gas constant and calculate its value in that unit. 2

(c) At constant pressure and temperature, what is the relation between the rate of diffusion of a gas and its molecular weight? 2

(d) An oxygen cylinder contains gas at a pressure of 10.3 atmosphere. Another oxygen cylinder of one-third capacity has a pressure of 1.1 atmosphere. The two cylinders are connected. What will be the pressure of the mixed gases in the two cylinders? 4

2. (a) Is equivalent weight of an element always the same?

Deduce a relationship between atomic weight and equivalent weight of an element.

5.01 gm of a metallic oxide on reduction by hydrogen produces 4.41 gm of the metal. The specific heat of the metal is 0.055. What is the atomic weight of the metal? 1+2+3=6

(b) A cylinder contains 0.28 gm of ethylene. How many
  (i) moles of ethylene
  (ii) molecules of ethylene
  (iii) atoms of carbon
  (iv) atoms of hydrogen
are there in it? 4

3. (a) Aqueous solution of sodium bisulphate is acidic but aqueous solution of sodium bicarbonate is alkaline. Explain. 2

(b) Give one example each of :
  (i) amphoteric oxide
  (ii) basic salt. 2

(c) A solution of ferric chloride, on standing, gives a precipitate of ferric hydroxide. Explain with reasons. 2

(d) 40 ml of a sulphuric acid solution is required for titrating 2.65 gm of sodium carbonate dissolved in water, using methyl orange as indicator. What is the normality of the acid?

Explain whether there would have been any difference, if phenolphthalein, instead of methyl orange, were used as the indicator. 3+1=4

4. (a) In open air $Na_2CO_3 . 10 H_2O$ is efflorescent, while $MgCl_2 . 6H_2O$ is deliquescent. Explain with reasons. 2

(b) What is solubility? Is the solubility of sugar in a cup of water the same at Calcutta and at Darjeeling? Give reasons for your answer. 2

(c) How by a single experiment you can ascertain whether a particular solution is unsaturated, saturated or super-saturated? 2

(d) A bucket of turbid water does not become clear even on standing for a long time. Why?

How can you make this turbid water clear? 2

(e) Give one example of each of the following :
  (i) allotropy
  (ii) tribasic acid
  (iii) isomorphism
  (iv) emulsion. 2

5. (a) Deduce a relationship between chemical equivalent and electrochemical equivalent. 2

(b) When copper sulphate is electrolysed with copper electrodes, the anode loses its weight—Explain. 2

(c) What is meant by one Faraday of electricity? 2

(d) A current of 0.5 ampere is passed through a solution of copper sulphate for 20 minutes using platinum electrodes. Calculate

(i) the weight of copper deposited at the cathode

(ii) volume of oxygen liberated at the anode at N.T.P. 4

6. (a) What are meant by 'reversible reaction' and 'chemical equilibrium? What is the effect of catalyst on chemical equilibrium? 1+1+1=3

(b) Express the equilibrium constant of the reaction

N_2 (*gas*) + $3H_2$ (*gas*) $\rightleftharpoons$ $2NH_3$ (*gas*) in the forms K_p and K_c and find out the relation between them. 1+1+2=4

(c) State La Chatelier's principle and explain with its help the effect of change of pressure and temperature in the following reaction :

$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3 + 45{,}000$ Cal. 1+1+1=3

Group — B

Answer any *four* questions.

7. (a) Name a liquid metal and a solid non-metal. 1

(b) What is aqua regia? 1

(c) Name one bleaching agent and explain how it functions. 1

(d) Name a fertiliser containing both calcium and phosphorus. Write down its chemical formula. 1

(e) How is hardness of water expressed? 1

(f) Name two principal ingredients of coal gas. 1

(g) Give example of two gases combining to give a solid product. 1

(h) Name two allotropes of carbon. 1

(i) You are to dry the compounds on the right hand side with the help of compounds on the left hand side. Indicate your choice of the drying agent : 2

$CaCl_2$ (anhydrous)	NH_3
H_2SO_4 (conc.)	H_2S
CaO	HCl
P_2O_5	CO

8. Explain why : 5×2=10

(a) HNO_3 cannot be used for preparation of H_2S from FeS.

(b) H_2SO_4 cannot be used for preparation of CO_2 from marble.

(c) Nascent hydrogen is a stronger reducing agent than ordinary hydrogen.

(d) Silent electric discharge is passed in the preparation of ozone from oxygen.

(e) SO_3 gas is absorbed in 98% H_2SO_4 instead of water during the manufacture of sulphuric acid.

9. How do you prepare : $4\times 2\frac{1}{2} = 10$

(a) Nitric acid from ammonia

(b) Phosphorous from bone ash

(c) Fluorine from potassium hydrogen fluoride

(d) Borax from colemanite.

10. (a) Write down the chemical principle of borax bead test. 2

(b) Show that sulphuric acid many act as an oxidising agent. 2

(c) Show that ammonia may act as a reducing agent. 2

(d) Show that hydrogen peroxide may act as a reducing agent.

How is the strength of hydrogen peroxide expressed? 2+2=4

11. (a) Show that H_3PO_3 is a reducing agent. 2

(b) During preparation in the laboratory phosphene produces white fumes—Give reason. 2

(c) There are two unlabelled bottles in your laboratory—one containing dil H_2SO_4 and the other containing dil HCl. How do you identify them? 2

(d) How do you separate CO_2 and SO_2 from a mixture of the two? 2

(e) Write note on : Active nitrogen. 2

12. State with equation what happens when : 5×2=10

(a) Ammonia and carbon dioxide gases are passed into a mixture of powdered gypsum and water.

(b) Concentrated sulphuric acid is slowly added to a mixture of solution of ferrous sulphate and potassium nitrate.

(c) Nitrogen gas is passed over heated calcium carbide and the resulting compound is heated with water.

(d) Manganese dioxide powder is heated with conc. hydrochloric acid.

(e) Ammonia solution is added slowly to a solution of silver nitrate.

JT. ENT. CHEMISTRY : 2000

1. (a) Radioactive element $^{227}_{89}Ac$ undergoes a series of disintegration and finally yields $^{207}_{82}Pb$. What is the minimum numbers of α and β particles involved in this disintegration? 1

(b) How many elements are called lanthanides? Indicate their general electronic configuration. 1

(c) Name two solid elements which on combination give a liquid compound. Name the compound also. 1

(d) $^{238}_{92}U + ^{1}_{0}n \longrightarrow A \longrightarrow B + 2\beta^-$,

$^{232}_{90}Th + ^{1}_{0}n \longrightarrow C \longrightarrow D + 2\beta^-$

Identify A, B, C, D. $\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}$

2. Arrange the following according to the instructions given :

(a) K, Li, Na (increasing order of atomic size) $\frac{1}{2}$

(b) HI, HCl, HBr (increasing order of acid strength) $\frac{1}{2}$

(c) Na, Cu, Zn (increasing electropositive character) $\frac{1}{2}$

(d) H_2, Cl_2, CH_4 (increasing order of diffusion) $\frac{1}{2}$

(e) PH_3, AsH_3, NH_3 (increasing order of stability and the acid character) $\frac{1}{2}$

(f) Cu, S, graphite (increasing order of electrical conductivity) $\frac{1}{2}$

3. (a) The weight of 350 ml of a diatomic gas at 0°C and 2 atm, pressure is 1 g. Calculate the weight of its one atom. 2

(b) Ammonia under a pressure of 15 atm. at 27°C is heated to 347°C in a closed vessel in the presence of a catalyst. Under these conditions, NH_3 is partially decomposed according to the equation : $2NH_3 \rightleftharpoons N_2 + 3H_2$.

The vessel is such that the volume remains constant whereas the pressure increases to 50 atm. Calculate the % of NH_3 actually decomposed. 3

4. Give S.I. definition of mole. 1

(b) "Molecular mass of hydrogen sulphide is 34"—elucidate. $1\frac{1}{2}$

(c) Ca^{2+}, K^+, S^{2-}, Cl^- have 18 extranuclear electrons. How will they be arranged in the increasing order of size? 1

(d) Give an example of 'diagonal relationship' in periodic table. Why is it observed? $1\frac{1}{2}$

5. (a) Calculate the pressure of Argon vapour in a vacuum tube in microtorr when 3×10^4 atoms are present in a volume of 5 ml at –100°C. 3

(b) Which one has minimum dipole moment? Butene—1, cis-Butene—2, trans-Butene—2, 2-methyl propane. 1

(c) Which one has unpaired electron? KO_2, AlO_2^{-1}, BaO_2, NO_2^{+1} 1

6. (a) 3.15 gms of $(COOH)_2 . xH_2O$ are dissolved in water and the volume is made up to 500 ml. On titration, 16.68 ml of the solution are required for exact neutralisation of 50 ml of $\left(\frac{N}{30}\right)$ NaOH solution. Calculate the value of x. 3

(b) Give one example of solid aerosol and one liquid aerosol. Justify your answer. $\frac{1}{2}+\frac{1}{2}$

(c) Define isoelectric point of colloid. 1

7. (a) 2.00 gm of a mixture of sodium carbonate and bicarbonate loses 0.248 gm when heated to 300°C. Calculate the percentage of sodium carbonate in the mixture. 2

(b) Neither pure H_2SO_4 nor pure $HClO_4$ conducts electric current but a mixture of two does.—Explain. 1

8. (a) Which of the following species does Bohr's theory apply to?

(i) H^+, (ii) He^+, (iii) Li^+, (iv) Li^{2+}, (v) Be^{2+}, (vi) Be^{3+} $1\frac{1}{2}$

(b) If a '5g' orbital be there, what would be the maximum number of electrons it can accommodate? $\frac{1}{2}$

(c) Why are ionic compounds usually high melting and covalent compounds low? Why has diamond a very high melting point? 3

9. State with balanced equations what happens when :

(a) Cl_2 is passed through KI solution. Excess Cl_2 is again passed through the solution. 1+1

Complete and balance the following equations :

(b) $KNO_3 + FeSO_4 + H_2SO_4$ (conc.) = 1

(c) $H_2S + K_2CrO_4 + H_2SO_4 =$ 1

(d) $Al + KMnO_4 + H_2SO_4 =$ 1

10. (a) A solution contains Na_2CO_3 and $NaHCO_3$. 10 ml of the solution requires 2.5 ml of 0.1 M-H_2SO_4 for neutralisation using phenolphthalein as an indicator. Methyl orange is then added when a further 2.5 ml of 0.2 M-H_2SO_4 was required. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in one litre of the solution. 3

(b) Which molecules of the following will be polar? H_2S, BCl_3, CCl_4, C_2H_6 and CO. 1

(c) Which molecules of the following would you expect to show hydrogen bonding? CH_4, HCl, HCOOH, C_6H_6, pure HNO_3. 1

11. (a) Chlorine is prepared in the laboratory by heating manganese dioxide with c. hydrochloric acid. But a brown colour develops with evolution of little chlorine before heating. What is it due to? What happens when heat is applied? Give equations. 2

(b) Identify the lettered compounds : 2

$$\text{Colemanite} \xrightarrow[\text{(excess)}]{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[1200^0C]{NH_4Cl} C \xrightarrow{HF} D$$

(c) What are *stalactites* and *stalagmites*? 1

12. (a) Barium nitrate and calcium chloride were mixed in water to form a solution 'X'. Potassium chromate and sodium chloride were mixed in water to form a solution 'Y'. What would happen if 'X' and 'Y' are now mixed? 1

(b) In an examination on qualitative analysis a candidate had been supplied with a white salt that became yellow when hot and white in cold; in wet test he made a mistake and got a white precipitate in group IIIA. What the basic radical was? What mistake did he commit? 1

(c) What happens when a paper soaked in mercurous nitrate solution is held in ammonia? Give equation. 1

(d) What are fossil fuels? Why are they so called? 1

13. (a) Anhydrous magnesium chloride cannot be obtained by heating hydrated magnesium chloride—why? 1

(b) Give two important uses of sodium cyanide. 1

(c) Name two chemicals which are used to remove dissolved oxygen in boiler feed water. 1

(d) Hydrofluoric acid cannot be stored in glass container. Why? 1

(e) Name two isomers of hydrogen. How do they differ from each other? 1

14. (a) During preparation of phosphine gas, coal gas or CO_2 is passed through reaction vessel. Why? 1

(b) Sodium carbonate is manufactured by Solvay process but potassium carbonate cannot be manufactured by this process. Why? 1

(c) What happens when (write visible changes and equations)

(i) H_2S is passed into a solution of sodium ethoxide in anhydrous alcohol.

(ii) Potassium persulphate is added to a solution of silver nitrate.

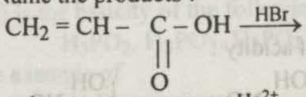
(iii) Borax is heated. 1×3

15. (A) is a light green water-soluble crystalline substance. On heating gradually it becomes white, brown and finally red (D), along with evolution of two gases (B) and (C). The red solid (D) imparts yellow and green colours to a borax-bead in oxidising and reducing flames respectively. Aqueous solution of (A) turns acidified potassium dichromate solution green. The gas mixture (B and C) decolourises $KMnO_4$ solution. Identify (A), (B), (C), (D) and explain the observations. 4

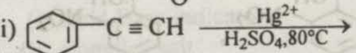
16.(a) Write only structures of the products of ozonolysis of 0-xylene (1, 2-dimethyl benzene). 1

(b) How many alkenes may be obtained on treatment of 2-bromobutane with alcoholic KOH? Name them. $1\frac{1}{2}$

(c) Name the products :

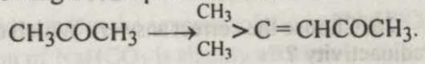
(i) 

$CH_2=CH-\underset{\underset{O}{||}}{C}-OH \xrightarrow{HBr} ?$ (ii) Potassium propionate $\xrightarrow{electrolysed} H_2 + ?$

(iii) 

$1\frac{1}{2}$

(d) Name the reactions involved in the following one-step conversions :

(i) PhOH $\longrightarrow$ salicylaldehyde; (ii) 

$CH_3COCH_3 \longrightarrow \overset{CH_3}{\underset{CH_3}{>}}C=CHCOCH_3$. 1

17. Answer the following :

(a) When passed over heated copper at 300°C, an organic compound was found to give an olefin. The organic compound is most likely to be

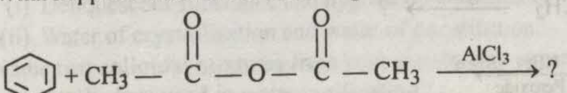
(i) primary alcohol, (ii) alkane, (iii) secondary alcohol, (iv) alkyne, (v) tertiary alcohol. 1

(b) Marsh gas mainly contains : C_2H_2, CH_4, H_2S, CO, none. 1

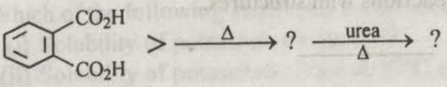
(c) On ozonolysis 'A' gives a molecule of acetone and 1 molecule of formaldehyde. 'A' is :

(i) Propylene, (ii) Ethylene, (iii) n-Butylene, (iv) Isobutylene. 1

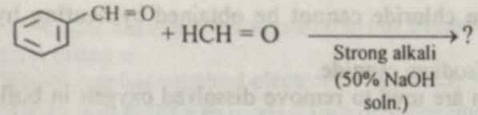
18. What happens when in the following reactions (show the products)?

(a) 

1

(b) 

$\frac{1}{2} + \frac{1}{2}$

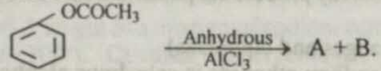
(c) 

1

(d) Write down the bond angles and structures of C_2H_4, C_2H_2. $\frac{1}{2}+\frac{1}{2}$

(e) How do you chemically distinguish between (i) n-hexanol and phenol. (ii) n-hexylamine and aniline. $\frac{1}{2}+\frac{1}{2}$

19. (a) Name two isomeric dicarboxylic acids having general formula $C_4H_6O_4$. Show their structures also. 1+1

(b) 

Identify A and B. $\frac{1}{2}+\frac{1}{2}$

20. How would you convert (arrow equations only)? 1×5

(a) Benzaldehyde into cinnamic acid.

(b) Butyric acid to α-chlorobutyric acid.

(c) Benzene into phenylhydrazine.

(d) One polyhydric alcohol into acrolein.

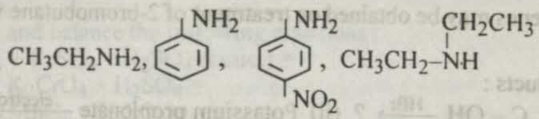
(e) Acetaldehyde into lactic acid.

21. Which element has the highest electronegativity and which one has lowest? 1

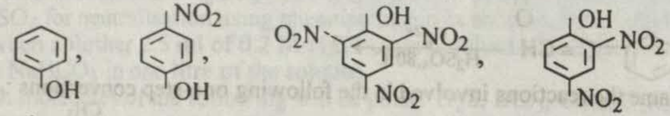
22. Why alum is used for clarification of muddy water? 1

23. Name one biodegradable polymer and one non-biodegradable polymer. 1

24. Arrange in order of increasing basicity : 1



25. Arrange the following in increasing order of acidity : 1



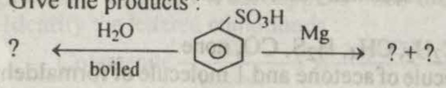
1

26. Choose the correct answer : Which of the following is not a unit for measurement of radioactivity ? 1

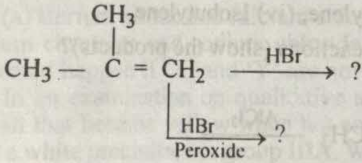
(A) Curie, (B) Becquerel, (C) Rutherford, (D) Fermi.

27. Name (IUPAC method) any aldehyde (aliphatic) other than formaldehyde that responds to Cannizaro reaction. 1

28. Give the products : 1



29. Name two coal based gaseous fuels. Which one has higher calorific value? 1

30. 

1

Show the products of the above reactions with structures. $\frac{1}{2}+\frac{1}{2}$

H. S. CHEMISTRY : 2001

First Paper

Group — A

Answer any ***four*** questions.

1. (a) Is the weight of an atom and atomic weight of an element synonymous? How many molecules of carbon dioxide are there in 1 millimole of carbon dioxide? What do you mean by atomic mass unit? 2+1+1=4

(b) Chlorine and oxygen form two different compounds. In one compound there is 81.6% and in another compound 59.7% chlorine by weight. State the law of chemical combination which is consistent with this data. Give reasons for your answer. 4

(c) What is the difference between the equations $PV = RT$ and $PV = nRT$? 2

2. (a) What is the difference between the equivalent weight and gram-equivalent of an element?

Find out the equivalent weight :

(i) nitrate radical

(ii) sodium carbonate.

When will the equivalent weight and atomic weight of an element be same? 1+1+1=3

(b) The oxide of an element contains 53 percent of the element. The vapour density of the chloride of the element is 66. Find out the atomic weight of the element. 3

(c) Give example of two isomorphous crystals.

Give one example of polymorphism. 1+1=2

(d) Mention two limitations of Dulong-Petit's law. 2

3. (a) Is the basicity of the following acids the same?

H_3PO_2, H_3PO_3, H_3PO_4

Give example of

(i) Acid-Base indicator

(ii) Complex salt 1+1=2

(b) Explain why : 1+1+1+1=4

(i) Both $NaHSO_4$ and $NaHCO_3$ are acid salt. But the aqueous solution of $NaHSO_4$ is acidic, while the aqueous solution of $NaHCO_3$ is slightly alkaline.

(ii) BaO_2 is called Barium peroxide but MnO_2 is called Manganese dioxide.

(iii) The strength of NaCl solution is expressed in formality, not in molarity.

(iv) Calcium carbonate is formed when sodium carbonate is added into calcium chloride solution; but ferric carbonate is not formed similarly when sodium carbonate is added into ferric chloride solution.

(c) 25 c.c. of 0.5 N HCl is added into 50 c.c. of 0.8% NaOH solution. What will be the acidic or basic strength of the resultant solution in normality? 4

4. (a) Distinguish with example : 2

(i) Deliquescent substance and hygroscopic substance.

(ii) Water of crystallisation and water of constitution.

(b) Name two colloidal mixtures from your day-to-day experience.

Why is potash alum used in water purification? 1+1=2

(c) Which of the following statements is correct and why?

(i) Solubility of potassium nitrate is 65.

(ii) Solubility of potassium nitrate at 40°C is 65 gm.

(iii) Solubility of potassium nitrate at 40°C is 65.

75 c.c. of the saturated solution of a substance at 40°C contains 15 gms of the substance. If the specific gravity of the solution is 1.2, what is the solubility of the substance at that temperature? 1+3=4

(d) State four utilities of the solubility curve. 2

5. (a) Write down the names of the products of electrolysis of the following :

Fused sodium chloride, dilute sodium chloride solution, concentrated sodium chloride solution. 3

(b) Deduce a relation among Faraday (F). Avogadro number (N) and electronic charge (e), and calculate from it the amount of charge of an electron. 3

(c) How many amperes of electric current is necessary to produce 0.406 gm and copper in 30 minutes from copper sulphate solution?

[Given at wt. of Cu = 63.5] 4

6. (a) Reaction of water vapour and red-hot iron is conducted first in a closed vessel and then in an open vessel. Will the amount of the products be the same in both the cases? 1

(b) State the law of mass action and deduce from this the equilibrium constant of a reversible reaction. 1+2=3

(c) When is equilibrium constant expressed by K_p and when by K_c? When will the value of K_p and K_c be the same? 1+1+1=3

(d) Describe with the help of Le Chatelier's principle, the influence of temperature, pressure and catalyst on the preparation of ammonia by Haber's process. 1+1+1=3

Group — B

Answer any *four* questions.

7. (a) Name two fertilisers containing nitrogen. 1

(b) Write down the chemical identity of the following substances :

Oleum, liquor ammonia, dry ice, baking powder, Nessler's reagent and producer gas. 3

(c) How do fire extinguisher and safety match function? 3

(d) What are greenhouse gases? What are their adverse effects?

Why does acid rain occur? 2+1=3

8. (a) What is the difference between soft water and deionised water? 1

(b) How do you ascertain whether a colourless liquid is water or not? 1

(c) 0.001 mole $MgSO_4$ is dissolved in 1 litre water. Find out the hardness of the water. 2

(d) How does water react with the following substances? 3

Sodium, Calcium carbide, Phosphorus trioxide.

(e) Give examples of the activity of occluded hydrogen and nascent hydrogen.

What is the difference between ortho-hydrogen and para-hydrogen? 2+1=3

9. How do you convert? 5×2=10

(a) White phosphorus into red phosphorus and vice versa.

(b) Borax into boric acid and vice versa.

(c) Nitrogen into ammonia and vice versa.

(d) Carbon dioxide into carbon monoxide and vice versa.

(e) Ammonia into nitric acid and vice versa.

10. (a) Why are hydrated barium peroxide and dilute sulphuric acid used in the preparation of hydrogen peroxide by reaction of barium peroxide and sulphuric acid? Can hydrochloric acid be used in place of sulphuric acid? 2+1=3

(b) Give one example each of the acid property, oxidising property and reducing property of hydrogen peroxide. 3

(c) Express the strength of 20 volume hydrogen peroxide solution in gms/litre and in percentage strength. 2+1=3

(d) How do you know whether a liquid is hydrogen peroxide or not? 1

11. State with equation what happens when : 5×2=10

(a) A mixture of the aqueous solution of sodium nitrite and ammonium chloride is heated.

(b) White phosphorous is heated with a concentrated solution of potassium hydroxide.

(c) Chlorine gas is passed through an aqueous solution of iodine.

(d) A mixture of phosphorus and concentrated nitric acid is heated.

(e) Ozone gas is passed into an aqueous solution of potassium iodide.

12. (a) How do you distinguish between? 1+1=2

(i) Nitrite salt and nitrate salt.

(ii) Sulphite salt and sulphate salt.

(b) What happens when orthoboric acid is slowly heated?
How is orthoboric acid detected? 2+1=3

(c) How do you separate the gases from the following gas mixtures? 2+2=4

(i) CO and CO_2

(ii) N_2O and NO.

(d) What is 'fuming nitric acid'? 1

JT. ENT. CHEMISTRY : 2001

1. (a) If the electron in the H-atom approaches the nucleus in a continuous manner, what type of spectra will be observed from the emitted energy? 1

(b) An element has atomic number 35. Write its electron configuration and what will be its position in Periodic Table. What are the possible stable oxidation states of the element? 2

(c) In H-atom, the energy of the electron in the nth orbit is given as $E_n = -\frac{13.6}{n^2}$ ev.

Show that $E_{(n+1)} - E_n = \frac{13.6 \times 2}{n^3}$ ev for large values of n. 3

(d) Why is the element $_{92}U^{238}$ radioactive? Some artificial radio-isotopes may be positron (e^+) emittor. How such emission may take place? Mention a property of some elements which is not periodic in nature. 4

2. (a) Write the oxidation states of C-1 and C-2 in CH_3CH_2OH. 1

(b) What is the equivalent weight of $KH(IO_3)_2$ as an oxidant in presence of 4.0 (N) HCl when ICl becomes the reduced form? (K = 39.0, I = 127.0) 2

(c) Show that when the mole-fraction of the solvent in a solution is nearly unity, the molarity (c) and molality (m) of the solution are connected by the equation

$$c = \rho \times m$$

where ρ = density of the solution. 3

(d) The density of copper is 8.94 gms/c.c. Find out the number of coulombs of electricity needed to plate an area of 10 cm × 10 cm to a thickness of 10^{-2} cm using copper sulphate solution as an electrolyte. (Cu = 63.5) 4

3. (a) What are the shapes of NH_3 and BF_3 molecules? 1

(b) Cane sugar is a covalent compound but it dissolves in polar solvent water—why? 1

(c) Which one of NF_3 and NH_3 is more polar and why? 2

(d) Cite one example (with balanced equation) of each of the following reactions : 2

(i) decomposition (ii) double decomposition
(iii) elimination (iv) rearrangement.

(e) A gaseous hydrocarbon has the empirical formula CH_2. At a given temperature and pressure, it has the density 3.86 gms/litre. At this condition oxygen has the density 2.21 gms/litre. Find out the molecular formula of the compound. 4

4. (a) What is the equivalent weight of ^{18}O? 1

(b) In which mode of expression, the concentration of a solution remains independent of temperature? 1

(i) Molarity (ii) Normality
(iii) Formality (iv) Molality.

(c) Basicity of H_3PO_2, H_3PO_3 and H_3PO_4 are same—justify or criticise. 3

(d) At a particular temperature, the number of moles of different constituents for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ are (1-α) for N_2, 3(1-α) for H_2 and 2α for NH_3. Find out Kp in terms of α and the total pressure. Show that α will increase with the increase of the total pressure. Assume that $\alpha << 1$. 5

5. (a) How will you convert SO_2 into H_2S? Give equations for the reactions involved. 2

(b) How would proceed to convert nitrogen di-oxide into NH_3 by using (i) $KMnO_4$ soln., (ii) Zn-dust, (iii) NaOH? Give equations for the reactions. 3

(c) Give the equation for the auto-oxidation of 2-ethyl anthraquinol to produce H_2O_2. Why is the process called auto oxidation? What is the advantage of this process? Give an example of a reaction with equation in which ozone acts as an oxidant but no oxygen is produced. Which element is a stronger oxidant than ozone? 5

6. (a) What is glacial phosphoric acid? 1

(b) Acidity of H_3PO_3 and H_3PO_4 acids are almost of same strength—Why? 2

(c) How would you detect iodide and bromide in presence of each other? 3

(d) How CO_2 is produced in fire extinguisher and baking powder? 4

7. (a) Why bauxite with high silica content cannot be purified by Bayer's process? 2

(b) What is rouge? Give the simplest method of its preparation. 1

(c) Give reasons :

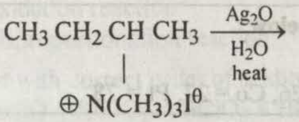
(i) No flux is used in the extraction of Zn by carbon reduction process.

(ii) $Fe_2(CO_3)_3$ is not obtained by reaction of $FeCl_3$ with Na_2CO_3.

(iii) In the extraction of copper no reducing agent is required. 3

(d) Zn can be extracted by electrolysis of $ZnSO_4$ solution. Can Al be extracted by electrolysing $Al_2(SO_4)_3$ solution? Discuss. 4

8. (a) Write the major product in the following reaction : 1



$$CH_3\,CH_2\,\underset{\underset{\oplus N(CH_3)_3I^{\ominus}}{|}}{CH}\,CH_3 \xrightarrow[\text{H}_2\text{O, heat}]{\text{Ag}_2\text{O}}$$

(b) Explain why the Grignard reagent from $BrCH_2C \equiv CH$ cannot be prepared. 2

(c) How many isomers of butene are possible? Indicate the type of isomerism among them. 2

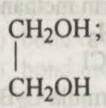
(d) How many isomers are possible for CH_2Cl_2 assuming carbon to have (i) rectangular planar geometry and (ii) square planar geometry? 2

(e) Why ethyl benzene is not prepared by simple alkylation of benzene? Devise a conveniant route for its synthesis. 3

9. (a) Give an example of the reaction where a Grignard reagent acts as a reducing agent. 1

(b) Sodium metal can be used for drying diethyl ether, but not for an alcohol.—Explain. 1

(c) Study the compounds $\underline{\underline{A}}$ to $\underline{\underline{D}}$ and answer the following questions : 4

$\underline{\underline{A}}$ =  $\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$; $\underline{\underline{B}} = CH_3CO_2Na$; $\underline{\underline{C}} = (CH_3CO)_2O$; $\underline{\underline{D}} = CH_3CHO$

(i) Which one gives effervescence with $NaHCO_3$ solution?

(ii) Which one is oxidised by alkaline $KMnO_4$ to a solid product?

(iii) Which one is a strong electrolyte?

(iv) Which one gives an orange-yellow precipitate with Brady's reagent?

(d) How would you carry out the following conversions as indicated? 4

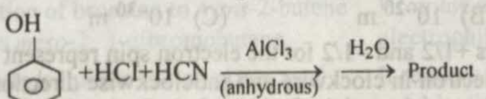
(i) Methanol from formaldehyde without using reducing agent;

(ii) Alkyl bromide to a primary alcohol having two more carbons than the bromide;

(iii) α-bromoacetic acid from acetic acid;

(iv) Acetaldehyde from acetone.

10. (a) What is the molecular weight of the product in the following reaction? 1



(b) What happens when chlorobenzene is treated with sodamide in liquid ammonia? 1

(c) Write the structure and name of the product when aniline and benzaldehyde is heated together. 1

(d) How will you obtain the following? 2

(i) Phenylhydroxylamine from benzene. (ii) Phenylhydrazine from aniline.

(e) How do you detect the presence of nitro group in an aromatic compound? Write the reaction(s). 2

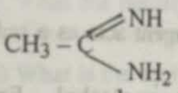
(f) Describe two reactions by which you can differentiate aniline from nitrobenzene. 3

I.I.T. CHEMISTRY (Screening Test) : 2001

Use the values of the constants as given below :
Planck's constant, $h = 6.626 \times 10^{-34}$ Js
Atomic Numbers : Cr = 24, Mn = 25, Fe = 26, Co = 27, Pt = 78

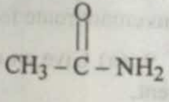
1. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because
(A) both are highly ionic
(B) one is oxidising and the other is reducing
(C) one of the steps is endothermic in both the cases
(D) all the steps are exothermic in both the cases

2. The correct order of basicities of the following compounds is


1

$CH_3-CH_2-NH_2$
2

$(CH_3)_2NH$
3


$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$
4

(A) $2 > 1 > 3 > 4$
(B) $1 > 3 > 2 > 4$
(C) $3 > 1 > 2 > 4$
(D) $1 > 2 > 3 > 4$

3. The compound that will react most readily with NaOH to form methanol is
(A) $(CH_3)_4N^+I^-$
(B) CH_3OCH_3
(C) $(CH_3)_3S^+I^-$
(D) $(CH_3)_3CCl$

4. The number of isomers for the compound with molecular formula $C_2BrClFI$ is
(A) 3 (B) 4 (C) 5 (D) 6

5. In thermodynamics, a process is called reversible when
(A) surroundings and system change into each other
(B) there is no boundary between system and surroundings
(C) the surroundings are always in equilibrium with the system
(D) the system changes into the surroundings spontaneously

6. In a solid 'AB' having the NaCl structure, 'A' atoms occupy the corners of the cubic unit cell. If all the face-centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
(A) AB_2 (B) A_2B (C) A_4B_3 (D) A_3B_4

7. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order
(A) 10^{-10} m (B) 10^{-20} m (C) 10^{-30} m (D) 10^{-40} m

8. The quantum numbers +1/2 and –1/2 for the electron spin represent
(A) rotation of the electron in clockwise and anticlockwise direction respectively
(B) rotation of the electron in anticlockwise and clockwise direction respectively
(C) magnetic moment of the electron pointing up and down respectively
(D) two quantum mechanical spin states which have no classical analogue

9. Which one of the following statements is false?
(A) Work is a state function
(B) Temperature is a state function
(C) Change in the state is completely defined when the initial and final states are specified
(D) Work appears at the boundary of the system

10. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as
(A) d^2 (B) d (C) $\sqrt{d}$ (D) $1/\sqrt{d}$

11. The reaction, $3ClO^-_{(aq)} \rightarrow ClO^-_{3(aq)} + 2Cl^-_{(aq)}$, is an example of

(A) oxidation reaction (B) reduction reaction

(C) disproportionation reaction (D) decomposition reaction

12. The set with correct order of acidity is

(A) $HClO < HClO_2 < HClO_3 < HClO_4$

(B) $HClO_4 < HClO_3 < HClO_2 < HClO$

(C) $HClO < HClO_4 < HClO_3 < HClO_2$

(D) $HClO_4 < HClO_2 < HClO_3 < HClO$

13. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is

(A) 40 ml (B) 20 ml (C) 10 ml (D) 4 ml

14. The number of S-S bonds in sulphur trioxide trimer (S_3O_9) is

(A) three (B) two (C) one (D) zero

15. The chemical composition of 'slag' formed during the smelting process in the extraction of copper is

(A) $Cu_2O + FeS$ (B) $FeSiO_3$

(C) $CuFeS_2$ (D) $Cu_2S + FeO$

16. The common features among the species CN^-, CO and NO^+ are

(A) bond order three and isoelectronic

(B) bond order three and weak field ligands

(C) bond order two and π-acceptors

(D) isoelectronic and weak field ligands

The questions below (17-21) consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the appropriate answer.

(A) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion*.

(B) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.

(C) If *assertion* is CORRECT, but *reason* is INCORRECT.

(D) If *assertion* is INCORRECT, but *reason* is CORRECT.

	Assertion **(column 1)**	***Reason*** **(column 2)**
17.	Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromobutane.	Bromine addition to an alkene is an electrophilic addition.
18.	Dimethylsulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.	It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.
19.	In any ionic solid [MX] with Schottky defects, the number of positive and negative ions are same.	Equal number of cation and anion vacancies are present.
20.	In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.	The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.
21.	Between $SiCl_4$ and CCl_4, only $SiCl_4$ reacts with water.	$SiCl_4$ is ionic and CCl_4 is covalent.

22. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is

(A) (molecular weight)/2
(B) (molecular weight)/6
(C) (molecular weight)/3
(D) same as molecular weight

23. The complex ion which has no 'd' electrons in the central metal atom is

(A) $[MnO_4]^-$
(B) $[Co(NH_3)_6]^{3+}$
(C) $[Fe(CN)_6]^{3-}$
(D) $[Cr(H_2O)_6]^{3-}$

24. The set representing the correct order of first ionization potential is

(A) $K > Na > Li$
(B) $Be > Mg > Ca$
(C) $B > C > N$
(D) $Ge > Si > C$

25. The correct order of hybridization of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is

(A) dsp^2, dsp^3, sp^2 and sp^3
(B) sp^3, dsp^2, dsp^3, sp^2
(C) dsp^2, sp^2, sp^3, dsp^3
(D) dsp^2, sp^3, sp^2, dsp^3

26. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_s) with its solubility (S) is

(A) $L_s = S^{p+q}.\ p^p.\ q^q$
(B) $L_s = S^{p-q}.\ p^q.\ q^p$
(C) $L_s = S^{pq}.\ p^p.\ q^q$
(D) $L_s = S^{pq}.\ (pq)^{p-q}$

27. Saturated solution of KNO_3 is used to make 'salt-bridge' because

(A) velocity of K^+ is greater than that of NO_3^-
(B) velocity of NO_3^- is greater than that of K^+
(C) velocities of both K^+ and NO_3^- are nearly the same
(D) KNO_3 is highly soluble in water

28. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is

(A) LiCl > NaCl > KCl
(B) KCl > NaCl > LiCl
(C) NaCl > KCl > LiCl
(D) LiCl > KCl > NaCl

29. If 'I' is the intensity of absorbed light and 'C' is the concentration of *AB* for the photo-chemical process $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to

(A) C
(B) I
(C) I^2
(D) C.I

30. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2\ NO_2$ is expressed by $K_p = (4x^2P)/(1 - x^2)$, where P = pressure, x = extent of decomposition. Which one of the following statements is true?

(A) K_p increases with increase of P
(B) K_p increases with increase of x
(C) K_p increases with decrease of x
(D) K_p remains constant with change in P and x

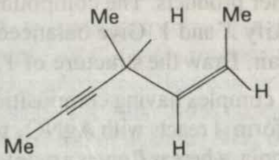
31. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives

(A) benzyl alcohol and sodium formate
(B) sodium benzoate and methyl alcohol
(C) sodium benzoate and sodium formate
(D) benzyl alcohol and methyl alcohol

32. An S_N2 reaction at an asymmetric carbon of a compound always gives

(A) an enantiomer of the substrate
(B) a product with opposite optical rotation
(C) a mixture of diastereomers
(D) a single stereoisomer

33. Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives



(A) an optically active compound
(B) an optically inactive compound
(C) a racemic mixture
(D) a diastereomeric mixture

34. The reaction of propene with HOCl proceeds via the addition of
(A) H^+ in the first step
(B) Cl^- in the first step
(C) OH^- in the first step
(D) Cl^+ and OH^- in a single step

35. 1-Propanol and 2-Propanol can be best distinguished by
(A) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
(B) oxidation with acidic dichromate followed by reaction with Fehling solution
(C) oxidation by heating with copper followed by reaction with Fehling solution
(D) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

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I.I.T. CHEMISTRY : 2001

Time : *Two hours* *Maximum marks* : 100

Note :
(i) There are 15 questions in this paper. Attempt ALL questions.
(ii) Answer each question starting on a new page. The corresponding question number must be written in the left margin. Answer all parts of a question at one place only.
(iii) Use only Arabic numerals (0, 1, 2,........, 9) in answering the questions irrespective of the language in which you answer.
(iv) Use of Logarithmic tables is permitted.
(v) Use of calculator is NOT PERMITTED.

Useful data :
Gas constant, $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
1 Faraday = 96,500 C mol^{-1}
1 C V = 1 J
Avogadro number, $N_A = 6.02 \times 10^{23}$
Planck constant, $h = 6.626 \times 10^{-34}$ J s
Speed of light, $c = 3.00 \times 10^8 \text{ m s}^{-1}$
Atomic number : B = 5; O = 8; K = 19; Co = 27; Cr = 24; Mn = 25
Atomic weight : H = 1.00; B = 10.81; C = 12.00; O = 16.00; Na = 23.00; K = 39.10; Mn = 55.00

1. Compound *X* on reduction with $LiAlH_4$ gives a hydride *Y* containing 21.72% hydrogen along with other products. The compound *Y* reacts with air explosively resulting in boron trioxide. Identify *X* and *Y*. Give balanced reactions involved in the formation of *Y* and its reaction with air. Draw the structure of *Y*. (5)

2. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms *A* and *B*. The form *A* reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas *B* gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of *A* and *B* and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). (5)

3. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parentheses (give reactions only) :

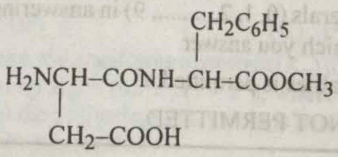
(i) silicon (1)
(ii) linear silicone containing methyl groups only (4)
(iii) Na_2SiO_3 (3) (5)

4. Hydrogen peroxide solution (20 ml) reacts quantitatively with a solution of $KMnO_4$ (20 ml) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolourised by 10 ml of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 ml of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate in molarity of H_2O_2. (5)

5. How would you synthesise 4-methoxyphenol from bromobenzene in *NOT* more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. (5)

6. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic *A*. The organometallic reacts with ethanal to give an alcohol *B* after mild acidification. Prolonged treatment of alcohol *B* with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (*C*). Write the structures of *A*, *B* and explain how *C* is obtained from *B*. (5)

7. Aspartame, an artificial sweetener, is a peptide and has the following structure :



$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad CH_2C_6H_5 \\ \qquad\qquad\qquad\qquad\quad | \\ H_2NCH\text{–}CONH\text{–}CH\text{–}COOCH_3 \\ \quad | \\ \quad CH_2\text{–}COOH \end{array}$$

(i) Identify the four functional groups.
(ii) Write the zwitterionic structure.
(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
(iv) Which of the two amino acids is more hydrophobic? (5)

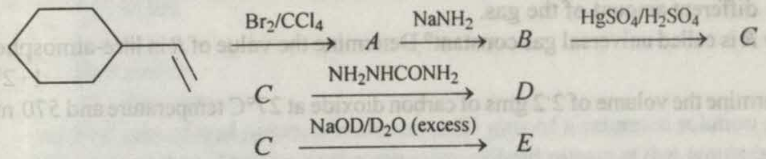
8. An alkene *A* ($C_{16}H_{16}$) on ozonolysis gives only one product *B* (C_8H_8O). Compound *B* on reaction with $NaOH/I_2$ yields sodium benzoate. Compound *B* reacts with KOH/NH_2NH_2 yielding a hydrocarbon *C* (C_8H_{10}). Write the structure of compounds *B* and *C*. Based on this information two isomeric structures can be proposed for alkene *A*. Write their structures and identify the isomer which on catalytic hydrogenation (H_2/Pd-C) gives a racemic mixture. (5)

9. The compression factor (compressibility factor) for one mole of a van der Waals gas at 0°C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant *a*. (5)

10. The rate of a first-order reaction is 0.04 mol litre^{-1} s^{-1} at 10 minutes and 0.03 mol litre^{-1} s^{-1} at 20 minutes after initiation. Find the half life of the reaction. (5)

11. A white substance *A* reacts with dilute H_2SO_4 to produce a colourless gas *B* and a colourless solution *C*. The reaction between *B* and acidified $K_2Cr_2O_7$ solution produces a green solution and a slightly coloured precipitate *D*. The substance *D* burns in air to produce a gas *E* which reacts with *B* to yield *D* and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH_3 or NaOH to *C* produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify *A*, *B*, *C*, *D* and *E*. Write the equations of the reactions involved. (10)

12. (a) Identify *A*, *B*, *C*, *D* and *E* in the following schemes and write their structures :



(b) Identify *X*, *Y* and *Z* in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound *Z* is treated with HBr and subsequently ozonolysed. **Mark the C* carbon in the entire scheme.**

$$BaC^*O_3 + H_2SO_4 \xrightarrow{\hspace{3em}} X \text{ (gas) [C* denotes } C^{14}]$$

$$CH_2 = CH\text{–}Br \xrightarrow[\text{(ii) } X \quad \text{(iii) } H_3O^*]{\text{(i) Mg/ether}} Y \xrightarrow{LiAlH_4} Z$$

(5+5)

13. When 1-pentyne (*A*) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (*A*), 95.2% 2-pentyne (*B*) and 3.5% of 1, 2-pentadiene (*C*). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria :

$$B == A \qquad \Delta G_1^\circ = ?$$

$$B == C \qquad \Delta G_2^\circ = ?$$

From the calculated value of ΔG_1° and ΔG_2° indicate the order of stability of *A*, *B* and *C*. Write a reasonable reaction mechanism showing all intermediates leading to *A*, *B* and *C*. (10)

14. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C.

$$Pt \mid H_2(g) \mid HCl(aq) \mid AgCl(s) \mid Ag(s)$$

(i) Write the cell reaction.

(ii) Calculate ΔH^0 and ΔS^0 for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.

(iii) Calculate the solubility of AgCl in water at 25°C. *Given*: The standard reduction potential of the $Ag^+(aq)/Ag(s)$ couple is 0.80 V at 25°C. (10)

15. The vapour pressure of two miscible liquids *A* and *B* are 300 and 500 mm of Hg respectively. In a flask 10 moles of *A* is mixed with 12 moles of *B*. However, as soon as *B* is added, *A* starts polymerising into a completely insoluble solid. The polymerisation follows first-order kinetics. After 100 minutes, 0.525 mole of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. *Assume* negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution. (10)

H. S. CHEMISTRY : 2002

First Paper

Group — A

Answer any *four* questions.

1. (a) What is the difference between 'density' and 'vapour density' of a gas? 1

(b) State with reasons whether the following statements are true or false : 3

(i) Volume fraction of an ideal gas in a mixture of ideal gases is equal to the mole fraction at the same temperature and pressure.

(ii) For a given ideal gas, the ratio of V/T at constant pressure is different for different amount of the gas.

(c) Why *R* is called universal gas constant? Determine the value of *R* in litre-atmosphere unit. 1+2=3

(d) Determine the volume of 2·2 gms of carbon dioxide at 27°C temperature and 570 mm pressure. 3

2. (a) What is the number of atoms in 1 mole of hydrogen? 1

(b) How many gram-molecules and how many grams of ammonia are present in 100 litres of ammonia at S.T.P.? 1

(c) How many atoms of hydrogen are present in a spherical drop of water of radius 1 mm? 2

(d) Determine the equivalent weight : 1

(i) Carbonate radical

(ii) Ferrous sulphate (Fe = 56)

(e) A gas mixture contains 80% N_2 and 20% O_2 by volume. Calculate the average vapour density of the gas mixture. 2

(f) Carbon combines with hydrogen to form three compounds *A*, *B* and *C*. Percentage of hydrogen in *A*, *B* and *C* are 25%, 14·3% and 7·7% respectively. Which one of the laws of chemical combination is in conformity with this example? 3

3. (a) Which one of the given pairs of compounds cannot co-exist in solution? 1

(i) $NaHCO_3$ and NaOH

(ii) Na_2CO_3 and $NaHCO_3$

(iii) Na_2CO_3 and NaOH

(iv) NaCl and $NaHCO_3$

(b) At first phenolphthalein and then glycerol is added to an aqueous solution of borax. Write down your observation and inference. 2

(c) In aqueous solution, H_3PO_4 is a tribasic acid but H_3PO_3 is a dibasic acid. Explain why. 2

(d) The formula of an oxide is MO_2. How do you know whether the oxide is a dioxide or a peroxide? 2

(e) 1 gm of pure $CaCO_3$ is completely dissolved in 40 ml of hydrochloric acid solution. 40 ml of 0·5 N NaOH solution is required to neutralise fully the solution thus formed. Determine the strength of the hydrochloric acid. 3

4. (a) Choose the correct answer : 1

With increase in temperature the solubility of sodium sulphate in water

(i) increases

(ii) decreases

(iii) remains unaltered

(iv) first increases and then decreases

(b) What is the essential difference between 'osmosis' and 'diffusion' in case of a solution? 1

(c) Why are some crystals efflorescent while some are deliquescent?

Give one example of each of efflorescent crystal, deliquescent crystal, hygroscopic crystal and hydrated crystal. 3

(d) What is the difference between a true solution and a colloidal solution?

Which of the following substances are colloidal solution?

(i) milk

(ii) blood

(iii) dew

(iv) smoke

(v) rain water 3

(e) 19·8 gms of lead nitrate are present in 50 gms of a saturated solution of lead nitrate at 35°C temperature. Determine the solubility of lead nitrate at that temperature. 2

5. (a) Chemical equivalent of sodium is 23. What is its electrochemical equivalent?

How many grams of sodium will be deposited at the electrode by one Faraday of electricity? 2

(b) What are the substances produced at the electrodes when copper sulphate solution is electrolysed using platinum electrode and copper electrode respectively? 2

(c) Using Faraday's laws, how can you determine the amount of the charge of a Cu^{+2} ion? 2

(d) 0·75 ampere electricity is passed through the aqueous solution of a metallic salt for 45 minutes, the weight of the cathode is increased by 0·6662 gm. Determine the equivalent weight of the metal. 4

6. (a) What do you mean by a 'chemical equilibrium'? Why is it called a 'dynamic equilibrium'? What is the effect of catalyst on chemical equilibrium? 3

(b) State Le-Chatelier's principle. Discuss the effect of changes in pressure and temperature on the following equilibrium :

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3 + 45\text{ K. Cal}$$

Establish the relationship between K_p and K_c for this equilibrium. 4+3

Group — B

Answer any *four* questions.

7. (a) Give example of two gases combining to give a solid product. 1

(b) Name a liquid metal and a solid non-metal. 1

(c) How do you prepare ammonium sulphate without using sulphuric acid? 2

(d) How will you remove hydrofluoric acid from a mixture of hydrofluoric acid and fluorine? 2

(e) Calculate the hardness of water sample which contains 1 mg of $CaCl_2$ per litre of water. 2

(f) Express the strength of '5-volume' hydrogen peroxide in percentage strength. 2

8. (a) How would you prepare dilute sulphuric acid from concentrated sulphuric acid? 1

(b) Give example of additive compounds formed by NO and CO. 1

(c) How is boric acid identified? 2

(d) How will you detect $CO_3^{=}$ and $SO_4^{=}$ in the laboratory? 2

(e) Name two bleaching agents. 1

(f) There is a mixture of carbon dioxide and carbon monoxide gas. How can you
   (i) convert the gas mixture fully to carbon dioxide?
   (ii) convert the gas mixture fully to carbon monoxide?
   (iii) remove carbon dioxide from the gas mixture? 3

9. State with equations what happens when : 5×2=10

(a) Sulphur dioxide gas is passed into concentrated nitric acid for sometime and then barium chloride solution is added into the mixture.

(b) Phosphonium chloride is heated with caustic soda solution and the gas obtained is passed through acidified copper sulfate solution.

(c) Nitrogen gas is passed over hot calcium carbide and the product obtained is heated with water.

(d) Chlorine is reacted with excess of ammonia.

(e) Mixture of boric acid and calcium fluoride is heated in presence of conc. H_2SO_4 and the compound produced is burnt in the non-luminous flame of Bunsen burner.

10. Prove with example : 5×2=10

(a) Nitrous acid acts as an oxidising agent.

(b) Hydrogen peroxide acts as a reducing agent.

(c) Sulphur dioxide acts as an oxidising agent.

(d) Nascent hydrogen is a more powerful reducing agent than ordinary hydrogen.

(e) Phosphorous acid has reducing power.

11. (a) A gaseous hydride produces a deep blue colouration when passed in excess through copper sulphate solution. The hydride is absorbed by fused calcium chloride. Write the two reactions with equations and identify the hydride. How hydrogen can be obtained from this hydride? Give equations. 2+1+2=5

(b) How does sulphur dioxide pollute the environment? 1

(c) How do you prepare? 2+2=4
   (i) Urea from ammonia
   (ii) Anhydrous hydrofluoric acid

12. (a) Describe the manufacture of nitric acid by Ostwald process. 4

(b) What is active charcoal and active nitrogen? 1

(c) Give the name of an oxide that forms two oxyacids in aqueous solution. 1

(d) Why hydrogen sulphide gas cannot be dried by passing through concentrated sulphuric acid? 2

(e) Why hydrobromic acid cannot be prepared by heating sodium bromide with concentrated sulphuric acid? 2

JT. ENT. CHEMISTRY : 2002

1. (a) Complete the equation : $^{238}_{92}U + ^{12}_{6}C \longrightarrow ^{244}_{98}Cf + \underline{\qquad\qquad}$. 1

(b) Hydrogen atom has only one electron but its spectrum shows many lines. Why? 2

(c) Explain why the α-particles were scattered by the gold-foil in Rutherford's gold-foil experiment, and yet the same α-source can cause a nuclear reaction with $^{9}_{4}Be$. Point out the significance of the two experiments in the context of atomic structure. 3

(d) A, B, C and D are four elements in the same period of which A and B are S-block elements. B and D combine to form the compound $B^+ D^-$. C and D combine to produce the covalent compound CD_2.

(i) What is the formula of the compound formed by A and D?
(ii) What is the nature of the above compound?
(iii) Find out the formula and the nature of the compound formed by B and C. 4

2. (a) At temperature, T, and pressure P, two ideal gases, A and B are mixed. Show that the density, d of the mixture is given by $d = (X_A M_A + X_B M_B) \times \frac{P}{RT}$, where X_A, X_B are the molefractions and M_A, M_B are the molecular weights of the gases A and B respectively. 4

(b) Pure water and pure hydrogen chloride are non-conductors of electricity, but their mixture conducts electricity.—Explain. 2

(c) When 50 ml ethanol and 50 ml water are mixed, predict whether the volume of the solution is equal to, greater than or less than 100 ml. Explain briefly. Is the solution ideal or non-ideal? 2

(d) Balance by oxidation number method : 2

$Fe_3O_4 + CO \longrightarrow FeO + CO_2$.

3. (a) CH_3 is planar. Mention hybridisation of carbon atom in it. In which orbital the unpaired electron is present? 2

(b) CO_2 and N_2O are both linear molecules, but CO_2 is non-polar while N_2O is polar. Why? 2

(c) At 300 K and 2·0 atm. pressure, gaseous HF has the density of 4·87 gms/litre. What is the molecular weight? Account for any discrepancy observed in the value. 3

(d) 10 ml oxygen is added to a 30 ml mixture of carbon monoxide and carbon di-oxide and the mixture is now exploded by electric spark. When the produced gas mixture is shaken with caustic potash solution the remaining gas is 5 ml oxygen. Determine the quantity of the CO and CO_2 present in the mixture (by volume). All the volumes mentioned above are measured at N.T.P. 3

4. (a) Give an example of a metallic oxide which is not basic but acidic. 1

(b) A sodium carbonate solution of strength 0·408 M has a density of 1·0816 g/ml. Find the molality of the solution. 2

(c) The oxides of two metals (A and B) are isomorphous. The atomic weight of A is 52 and the relative density of its chloride is 79. The oxide of B contains 47·1% oxygen. Find the atomic weight of B. 3

(d) 0·635 gm Cu was dissolved in 5·0 ml hot 60% HNO_3 (Sp. gr. = 1·5). When the reaction came to an end, the volume of the solution was adjusted to 250·0 ml. What is the normality of the solution with respect to HNO_3? (Cu = 63·5) 4

5. (a) Why concentrated H_2SO_4 has very high viscosity? 1

(b) Identify A to D : 2

$$\text{A (green solid)} \xrightarrow[\text{heated}]{\text{strongly}} \text{B (gas)} + \text{C (gas)} + \text{D (brown residue)}$$

$$K_2Cr_2O_7 \text{ (aq. solution)} + \text{B} + \text{C} \longrightarrow \text{green coloured solution}$$

$$\text{B} + H_2SO_4 \text{ (concentrated)} \longrightarrow \text{oleum}$$

$$\text{D} + \text{carbon} \xrightarrow{\text{heat}} \text{CO} + \text{residue (magnetic substance)}$$

(c) Why CO is poisonous gas but CO_2 is not? Write their structures to explain. 3

(d) 560·0 ml oxygen at STP can be obtained from 16·0 ml of a H_2O_2 solution when treated with ozone. Find out the strength of solution in normality. What is the per cent strength of the solution? 4

6. (a) How borax is obtained from sodium metaborate? 1

(b) Give an example where two acidic substances react to form an alkaline substance. 1

(c) Hydrofluoric acid can form bifluorides but hydrochloric acid cannot form bichlorides. —Explain. 3

(d) Solid A on being heated to 250°C in an atmosphere of inert gas in presence of I_2 yields solid B. When B is treated with conc. HNO_3, a tribasic acid is obtained. When A is heated with conc. NaOH solution in an atmosphere of argon gas yields a gas mixture which when passed through a U-tube, kept in freezing mixture, liquid C is obtained and the other gas D passes out. C when comes in contact with air burns spontaneously, when D is passed through $CuSO_4$ solution, a ppt. E is obtained. Identify A to E and give equation. 5

7. (a) Why is chalconite roasted and not calcined while extracting copper from it? 1

(b) Write down the effect of heat on the following compounds : 4

(i) hydrated aluminium chloride
(ii) green vitreol
(iii) cupric oxide
(iv) gypsum

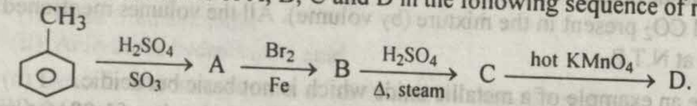
(c) What is the reducing agent of haematite in the blast furnace? What is tempering of steel? What is its utility? What is the role of limestone in the extraction of iron? 5

8. (a) How could you convert acetylene to dichloro acetaldehyde? 1

(b) The ozonide of an olefin on treatment with $LiAlH_4$ gives ethanol and propan-2-Ol. Draw the structure of the hydrocarbon and the ozonide. 2

(c) Write the structures of all possible isomeric alcohols of molecular formula $C_4H_{10}O$. How many π-diastereoisomers are possible in each case after dehydration? 3

(d) Write the structures of A, B, C and D in the following sequence of reactions : 4



9. (a) Write the name and structure of the ethyl ester of an aliphatic acid which on treatment with Grignard reagent gives a secondary alcohol. Logically support your answer. 2

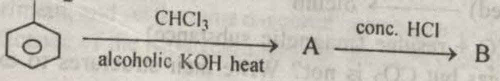
(b) Convert acetic acid to propanoic acid using diazomethane as one of the reagents. What is the name of this synthesis? 3

(c) Carry out (i) Williamson synthesis, (ii) Cannizzaro reaction, (iii) Hofmann degradation reaction utilising appropriate chemicals from the list given below. Write the structure of product(s) in each case : 5

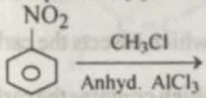
C_2H_5OH, C_6H_6, C_6H_5CHO, CH_3CHO, C_2H_5I, $C_6H_5NH_2$, CH_3CONH_2, Na, Zn(Hg), NH_2NH_2, Br_2, $AlCl_3$ (anhyd), NaOH, H_2SO_4

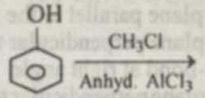
10. (a) What happens when phenol is treated with sodium in liquid ammonia? 1

(b) Give the structures and names of A and B in the following reactions : 2



(c) State whether the following reactions are feasible or not. If feasible, write the structure of the product(s). 2

(i) 

(ii) 

(d) Nitrobenzene on chlorination with Cl_2/Fe gives m-chloronitrobenzene; but chlorobenzene on nitration does not give the same product.—Explain. 2

(e) How do you convert aniline into nitrobenzene and benzoic acid without the intermediacy of benzene? 3

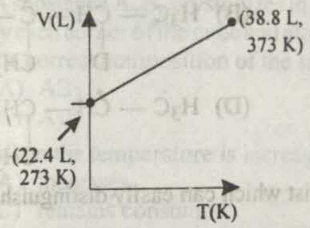
I.I.T. CHEMISTRY (Screening Test) : 2002

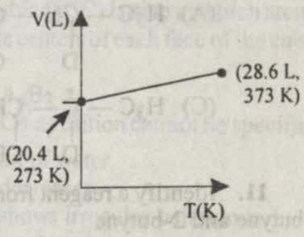
Useful data :
Mass of electron = $9{\cdot}108 \times 10^{-31}$ kg
Avogadro number = $6{\cdot}023 \times 10^{23}$
Gas constant R = $0{\cdot}082$ L atm K^{-1} mol^{-1}
Atomic number : Li = 3, Be = 4, B = 5, C = 6

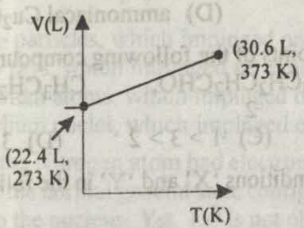
1. How many moles of electron weigh one kilogram?

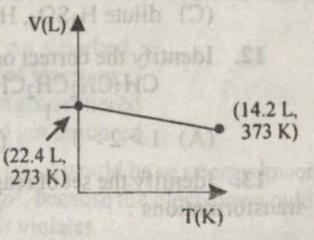
(A) $6{\cdot}023 \times 10^{23}$
(B) $\frac{1}{9{\cdot}108} \times 10^{31}$
(C) $\frac{6{\cdot}023}{9{\cdot}108} \times 10^{54}$
(D) $\frac{1}{9{\cdot}108 \times 6{\cdot}023} \times 10^{8}$

2. Which of the following volume (V) — temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?

(A) 

(B) 

(C) 

(D) 

3. Which of the following acids has the smallest dissociation constant?

(A) $CH_3CHFCOOH$
(B) FCH_2CH_2COOH
(C) $BrCH_2CH_2COOH$
(D) $CH_3CHBrCOOH$

4. Which of the following compounds exhibits stereoisomerism?

(A) 2-methylbutene-1
(B) 3 methylbutyne-1
(C) 3-methylbutanoic acid
(D) 2-methylbutanoic acid

5. The nodal plane in the π-bond of ethene is located in
(A) the molecular plane
(B) a plane parallel to the molecular plane
(C) a plane perpendicular to the molecular plane which bisects the carbon—carbon σ-bond at right angle
(D) a plane perpendicular to the molecular plane which contains the carbon—carbon σ-bond

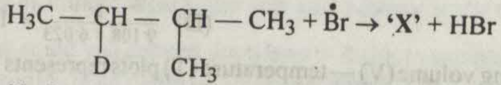
6. Polyphosphates are used as water softening agents because they
(A) form soluble complexes with anionic species
(B) precipitate anionic species
(C) form soluble complexes with cationic species
(D) precipitate cationic species

7. Identify the correct order of acidic strengths of CO_2, CuO, CaO, H_2O
(A) CaO < CuO < H_2O < CO_2 (B) H_2O < CuO < CaO < CO_2
(C) CaO < H_2O < CuO < CO_2 (D) H_2O < CO_2 < CaO < CuO

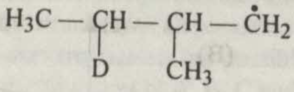
8. Identify the least stable ion amongst the following :
(A) Li^- (B) Be^- (C) B^- (D) C^-

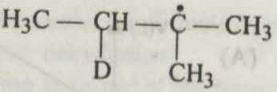
9. Which of the following molecular species has unpaired electron(s)?
(A) N_2 (B) F_2 (C) O_2 (D) O_2^{2-}

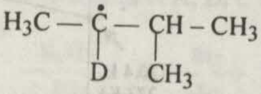
10. Consider the following reaction :

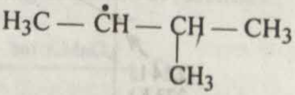

$H_3C-\underset{D}{CH}-\underset{CH_3}{CH}-CH_3+\dot{Br}\rightarrow \text{'X'}+HBr$

Identify the structure of the major product 'X'

(A)

$H_3C-\underset{D}{CH}-\underset{CH_3}{CH}-\dot{C}H_2$

(B)

$H_3C-\underset{D}{CH}-\underset{CH_3}{\dot{C}}-CH_3$

(C)

$H_3C-\underset{D}{\dot{C}}-\underset{CH_3}{CH}-CH_3$

(D)

$H_3C-\dot{C}H-\underset{CH_3}{CH}-CH_3$

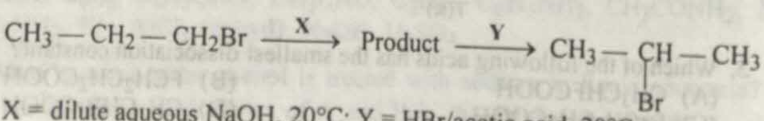
11. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne
(A) bromine, CCl_4 (B) H_2, Lindlar catalyst
(C) dilute H_2SO_4, $HgSO_4$ (D) ammoniacal Cu_2Cl_2 solution

12. Identify the correct order of boiling points of the following compounds :

$\underset{1}{CH_3CH_2CH_2CH_2OH}$, $\underset{2}{CH_3CH_2CH_2CHO}$, $\underset{3}{CH_3CH_2CH_2COOH}$

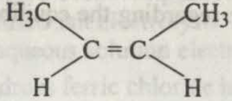
(A) 1 > 2 > 3 (B) 3 > 1 > 2 (C) 1 > 3 > 2 (D) 3 > 2 > 1

13. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations :


$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{Br}{CH}-CH_3$

(A) X = dilute aqueous NaOH, 20°C; Y = HBr/acetic acid, 20°C
(B) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(C) X = dilute aqueous NaOH, 20°C; Y = $Br_2/CHCl_3$ 0°C
(D) X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

14. Which of the following hydrocarbons has the lowest dipole moment?

(A) 

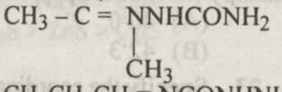
(B) $CH_3C \equiv CCH_3$

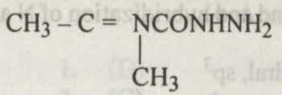
(C) $CH_3CH_2C \equiv CH$

(D) $CH_2 = CH - C \equiv CH$

15. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2$. HCl and sodium acetate gives a product 'C'. Identify the structure of 'C'

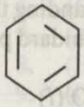
(A) $CH_3CH_2CH = NNHCONH_2$

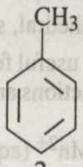
(B) 
$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = NNHCONH_2$

(C) 
$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = NCONHNH_2$

(D) $CH_3CH_2CH = NCONHNH_2$

16. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds :


1



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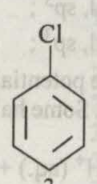

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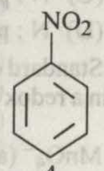


4

(A) 1 > 2 > 3 > 4

(B) 4 > 3 > 2 > 1

(C) 2 > 1 > 3 > 4

(D) 2 > 3 > 1 > 4

17. A substance A_xB_y crystallizes in a face centered cubic (FCC) lattice in which atoms 'A' occupy each corner of the cube and atoms 'B' occupy the centers of each face of the cube. Identify the correct composition of the substance A_xB_y

(A) AB_3

(B) A_4B_3

(C) A_3B

(D) Composition cannot be specified

18. When the temperature is increased, surface tension of water

(A) increases

(B) decreases

(C) remains constant

(D) shows irregular behaviour

19. Rutherford's experiment, which established the nuclear model of the atom, used a beam of

(A) β - particles, which impinged on a metal foil and got absorbed

(B) γ - rays, which impinged on a metal foil and ejected electrons

(C) helium atoms, which impinged on a metal foil and got scattered

(D) helium nuclei, which impinged on a metal foil and got scattered

20. If the Nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2\,2s^2\,2p^3$, because the electrons would be closer to the nucleus. Yet, $1s^7$ is not observed because it violates

(A) Heisenberg uncertainty principle

(B) Hund's rule

(C) Pauli exclusion principles

(D) Bohr postulate of stationary orbits

21. Consider the following equilibrium in a closed container :

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?

(A) neither K_p nor α changes
(B) both K_p and α change
(C) K_p changes, but α does not change
(D) K_p does not change, but α changes

22. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta U = 30.0$ L atm. The change in enthalpy (ΔH) of the process in L atm is

(A) 40·0
(C) 44·0
(B) 42·3
(D) not defined, because pressure is not constant.

23. Specify the coordination geometry around and hybridization of N and B atoms in a 1:1 complex of BF_3 and NH_3

(A) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3
(B) N : pyramidal, sp^3 ; B : pyramidal, sp^3
(C) N : pyramidal, sp^3 ; B : planar, sp^2
(D) N : pyramidal, sp^3 ; B : tetrahedral, sp^3

24. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below :

MnO_4^- (aq.) + 8 H^+ (aq.) + 5e^- → Mn^{2+} (aq.) + 4 H_2O (*l*) $E^0 = 1{\cdot}51$ V
$Cr_2O_7^{2-}$ (aq.) + 14 H^+ (aq.) + 6e^- → 2 Cr^{3+} (aq.) + 7 H_2O (*l*) $E^0 = 1{\cdot}38$ V
Fe^{3+} (aq.) + e^- → Fe^{2+} (aq.) $E^0 = 0{\cdot}77$ V
Cl_2(g) + 2e^- → 2 Cl^- (aq.) $E^0 = 1{\cdot}40$ V

Identify the only *incorrect* statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$

(A) MnO_4^- can be used in aqueous HCl
(B) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(C) MnO_4^- can be used in aqueous H_2SO_4
(D) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

25. Consider the chemical reaction, $N_2(g) + 3H_2(g) \rightarrow 2\,NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of N_2(g), H_2(g) or NH_3(g). Identify the correct relationship amongst the rate expressions

(A) Rate = $-d[N_2]/dt = -1/3\ d[H_2]/dt = 1/2\ d[NH_3]/dt$
(B) Rate = $-d[N_2]/dt = -3\ d[H_2]/dt = 2\ d[NH_3]/dt$
(C) Rate = $d[N_2]/dt = 1/3\ d[H_2]/dt = 1/2\ d[NH_3]/dt$
(D) Rate = $-d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

26. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y'.

(A) X = CO_2, Y = Cl_2
(B) X = Cl_2, Y = CO_2
(C) X = Cl_2, Y = H_2
(D) X = H_2, Y = Cl_2

27. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulfide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a

(A) Hg_2^{2+} salt (B) Cu^{2+} salt (C) Ag^+ salt (D) Pb^{2+} salt

28. Which of the following processes is used in the extractive metallurgy of magnesium?
(A) fused salt electrolysis (B) self reduction
(C) aqueous solution electrolysis (D) thermite reduction

29. Anhydrous ferric chloride is prepared by
(A) heating hydrated ferric chloride at a high temperature in a stream of air
(B) heating metallic iron in a stream of dry chlorine gas
(C) reaction of ferric oxide with hydrochloric acid
(D) reaction of metallic iron with hydrochloric acid

30. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium
(A) $CuS > ZnS > Na_2S$ (B) $ZnS > Na_2S > CuS$
(C) $Na_2S > CuS > ZnS$ (D) $Na_2S > ZnS > CuS$

• Answer Sheet •

1.	(D)	**16.**	(C)
2.	(C)	**17.**	(A)
3.	(C)	**18.**	(B)
4.	(D)	**19.**	(D)
5.	(A)	**20.**	(C)
6.	(C)	**21.**	(D)
7.	(A)	**22.**	(C)
8.	(B)	**23.**	(A)
9.	(C)	**24.**	(A)
10.	(B)	**25.**	(A)
11.	(D)	**26.**	(C)
12.	(B)	**27.**	(D)
13.	(B)	**28.**	(A)
14.	(B)	**29.**	(B)
15.	(A)	**30.**	(D)

I.I.T. CHEMISTRY : 2002

Time : *Two hours* *Maximum marks* : 60

Note :

(i) The Question Paper has 4 printed pages and has 12 questions. Please ensure that the copy of the Question Paper you have received contains all the questions.
(ii) Attempt ALL the questions. Each question carries 5 marks.
(iii) Answer each question starting on a new page. The corresponding Question Number must be written in the left margin.
(iv) Do not write more than one answers for the same question. In case you attempt a question more than once, please cancel the answer(s) you consider to be wrong. Otherwise, only the answer appearing last will be evaluated.
(v) Use only Arabic numerals (0, 1, 2, 3,.........., 9) in answering questions, irrespective of the language in which you answer.
(vi) Use of Calculator is NOT PERMITTED.
(vii) Use of Logarithmic Tables is PERMITTED.

Useful data :

Gas constant, $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Avogadro number, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

Planck constant, $h = 6.626 \times 10^{-34} \text{ Js}$

Boltzmann constant, $k_B = 1.38 \times 10^{23} \text{ J K}^{-1}$

Atomic number : B = 5, Al = 13, K = 19, Cr = 24, Fe = 26, Ni = 28, Cu = 29, Zn = 30

Atomic weight : H = 1.00, B = 10.81, C = 12.00, O = 16.00, Ni = 58.69

1. Five isomeric *para*—disubstituted aromatic compounds **A** to **E** with molecular formula $C_8H_8O_2$ were given for identification. Based on the following observations, give structures of the compounds.

(i) Both **A** and **B** form a silver mirror with Tollen's reagent; also, **B** gives a positive test with $FeCl_3$ solution.

(ii) **C** gives positive iodoform test.

(iii) **D** is readily extracted in aqueous $NaHCO_3$ solution.

(iv) **E** on acid hydrolysis gives 1, 4-dihydroxybenzene.

2. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH.

[Assume there is no change in volume on mixing; K_a of acetic acid is $1.75 \times 10^{-5} \text{ mol L}^{-1}$.]

3. Deduce the structures of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species.

4. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

(a) Determine (i) molecular weight, (ii) molar volume, (iii) compression factor (Z) of the vapour and (iv) which forces among the gas molecules are dominating, the attractive or the repulsive?

(b) If the vapour behaves ideally at 1000 K, determine the average translational kinetic energy of a molecule.

5. Write balanced equations for the reactions of the following compounds with water :

(i) Al_4C_3

(ii) CaNCN

(iii) BF_3

(iv) NCl_3

(v) XeF_4.

6. Identify **X, Y** and **Z** in the following synthetic scheme and write their structures.

$$CH_3CH_2C{\equiv}C{-}H \xrightarrow[\text{[ii] } CH_3CH_2Br]{\text{[i] } NaNH_2} \mathbf{X} \xrightarrow{H_2/Pd\text{-}BaSO_4} \mathbf{Y} \xrightarrow{\text{alkaline } KMnO_4} \mathbf{Z}$$

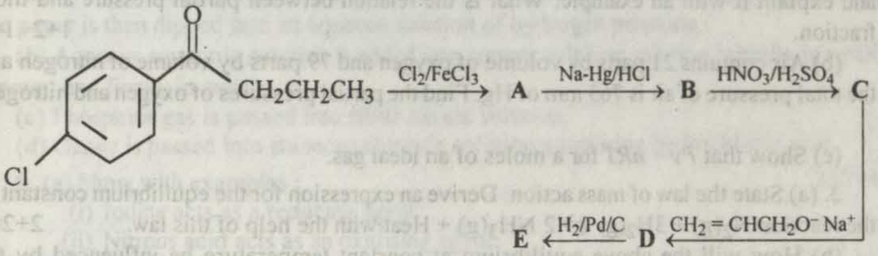
Is the compound **Z** optically active? Justify your answer.

7. How is boron obtained from borax? Give chemical equations with reaction conditions. Write the structure of B_2H_6 and its reaction with HCl.

8. ^{64}Cu (half-life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes.

9. When a white crystalline compound **X** is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, a reddish brown gas **A** is evolved. On passing **A** into caustic soda solution, a yellow coloured solution of **B** is obtained. Neutralizing the solution of **B** with acetic acid and on subsequent addition of lead acetate, a yellow precipitate **C** is obtained. When **X** is heated with NaOH solution, a colourless gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitate **D** is formed. Identify **A, B, C, D** and **X**. Write the equations of reactions involved.

10. Write structures of the products **A, B, C, D** and **E** in the following scheme.



11. A biologically active compound, Bombykol ($C_{16}H_{30}O$) is obtained from a natural source. The structure of the compound is determined by the following reactions.

(a) On hydrogenation, Bombykol gives a compound **A**, $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester;

(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O_3/H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.

Determine the number of double bonds in Bombykol. Write the structures of compound **A** and Bombykol. How many geometrical isomers are possible for Bombykol?

12. Two moles of a perfect gas undergo the following processes :

(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);

(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);

(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

(i) Sketch with labels each of the processes on the same P-V diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.

(iii) What will be the values of ΔU, ΔH, and ΔS for the overall process?

H. S. CHEMISTRY : 2003

First Paper

Group — A

Answer any *four* questions.

1. (a) State Gay Lussac's law of gaseous volumes. Explain the law with the help of Avogadro's hypothesis. 2+2=4

(b) Prove that at standard temperature and pressure the volume of one gram-mole of any gas is 22·4 litre. 2

(c) 0·6 gm of a metal on reacting with acid produces 560 ml hydrogen gas at N.T.P. 0·12 gm of the metal produces 0·20 gm of oxide when burnt. Again 0·56 gm of oxygen produces 0·63 gm of water. Show that the above facts can be explained with the help of one of the laws of chemical combination. [1 ml of Hydrogen gas at N.T.P. weighs 0·00009 gm] 4

2. (a) What is meant by partial pressure of a gas? State Dalton's law of partial pressure and explain it with an example. What is the relation between partial pressure and mole fraction. 1+2+1=4

(b) Air contains 21 parts by volume of oxygen and 79 parts by volume of nitrogen and the total pressure of air is 763 mm of Hg. Find the partial pressures of oxygen and nitrogen. 4

(c) Show that $Pv = nRT$ for a moles of an ideal gas. 2

3. (a) State the law of mass action. Derive an expression for the equilibrium constant of the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$ + Heat with the help of this law. 2+2=4

(b) How will the above equilibrium at constant temperature be influenced by the following changes? 4

(i) Hydrogen gas is added from outside.
(ii) Ammonia gas produced is removed from the system.
(iii) Helium gas is added from outside keeping the volume of the vessel unchanged.
(iv) A catalyst is added.

(c) What do you understand by 'solubility curve'? Explain with an example. 1+1=2

4. (a) Define equivalent weight of an element. Find out the relation between equivalent weight and atomic weight. 1+2=3

(b) State Dulong and Petit's law. What are its limitations. 2+1=3

(c) 0·1051 gm of a volatile liquid when vaporised in a Victor Meyer's tube, displaced 34·7 ml of air by displacement of water at 750 mm pressure and 27°C. Find the molecular weight of the liquid. (Aqueous tension at 27°C = 25 mm). Is it possible to determine the molecular weight of any volatile liquid by this method? Justify your answer. 3+1=4

5. (a) State Faraday's first law of electrolysis and give a definition of electrochemical equivalent from this law. Find the number of electrons whose total charge will be 1 coulomb. 1+1+2=4

(b) How many atoms of silver will be deposited at the cathode when 10 ampere current is passed for 5 hours through an aqueous solution of $AgNO_3$ (Ag = 108). 3

(c) Write a short note on : Dialysis. 3

6. (a) What is meant by neutralization? Why is an aqueous solution of Sodium Carbonate alkaline? Explain why phenolphthalein cannot be used in its titration. 2+2+1=5

(b) Give one example of each of the following : 3

(i) Superoxide

(ii) Basic salt

(iii) Double salt

(c) Find the normality of 47·5% nitric acid (Sp. gr. 1·30) 2

Group — B

Answer any *four* questions.

7. State with equations how will you prepare : 5×2=10

(a) Nitrogen from ammonium dichromate.

(b) Laughing gas from nitric acid.

(c) Carbon monoxide from sodium formate.

(d) Oxygen from barium peroxide.

(e) Orthophosphoric acid from bone ash.

8. State with equations what happens when : 5×2=10

(a) Hydrogen sulphide gas is passed over a filter paper soaked in lead acetate solution, the paper is then dipped into an aqueous solution of hydrogen peroxide.

(b) Aqueous ammonia solution is added into copper sulphate solution initially in small amount and finally in excess.

(c) Phosphine gas is passed into silver nitrate solution.

(d) Ozone is passed into stannous chloride solution containing hydrochloric acid.

9. (a) Show with examples : 2×2=4

(i) Iodine acts as a reducing agent.

(ii) Nitrous acid acts as an oxidising agent.

(b) Diamond is a non-conductor of electricity whereas graphite is a good conductor—Explain. 2

(c) How is atmospheric nitrogen fixed in soil? 2

(d) Explain with equations the principle of etching of glass. 2

10. (a) Give reasons why : 3×2=6

(i) Fluorine cannot be obtained by the electrolysis of anhydrous hydrofluoric acid or its aqueous solution.

(ii) Hydrogen iodide cannot be dried by using concentrated sulphuric acid.

(iii) Silent electric discharge is passed through oxygen to convert it into ozone.

(b) Distinguish by a chemical test between the following pairs of compounds : 2×2=4

(i) Hydrochloric acid and hydrobromic acid.

(ii) Sulphuric acid and sulphurous acid.

11. (a) Describe the manufacture of sulphuric acid by contact process. 4

(b) How will you remove traces of bromine mixed with hydrobromic acid? 1

(c) Compare the basic properties of NH_3 and pH_3. 2

(d) Name a non-metal which reacts with strong alkali to produce hydrogen gas. Write down the equation. Give one example of a reaction in which hydrogen act as an oxidising agent. 2+1=3

12. (a) What is meant by hardness of water? Explain the causes of hardness of water. Why is hard water unsuitable for boilers? 4

(b) A white solid "A" on treatment with dil. H_2SO_4 produces a colourless pungent smelling suffocating gas "B", which turns blue litmus solution red and discharges the blue colour of starch iodine paper. "B" on treatment with H_2O_2 solution produces "C" which gives a heavy white precipitate insoluble in acid, when treated with $BaCl_2$ solution. "B" reacts with sodium carbonate to produce a colourless odourless gas "D" and reproduces "A". Identify "A", "B", "C" and "D" and explain the reactions giving equations. 6

JT. ENT. CHEMISTRY : 2003

1. (a) Give the name and atomic number of the inert gas atom in which the total number of *d* electrons is equal to the difference between the numbers of total *p* and total *s* electrons. 2

(b) Classify the elements having atomic numbers as given below into 3 separate pairs on the basis of similar chemical properties. Give brief electronic explanation : 9, 12, 16, 34, 53, 56. 3

(c) (i) What do you mean by artificial radioactivity? Give an example. 2

(ii) $^{234}_{90}$Th disintegrates and ultimately gives $^{206}_{82}$Pb. How many α-and β-particles are emitted during the process? 2

(iii) Give the set of quantum numbers that describe an electron in a 3p orbital. 1

2. (a) What is the S.I. unit of dipole moment? 1

(b) Draw the Lewis dot diagrams for Nitric acid, Sulfuric acid, Phosphorous acid and Hypophosphorous acid. 2

(c) Explain why water at 1 atmosphere pressure has the highest density at 4°C. 2

(d) 1 gm of a mixture of calcium carbonate and magnesium carbonate gave on ignition 240 ml of carbon di-oxide at S.T.P. What is the percentage composition of the mixture? 5

3. (a) Milk is an emulsion. Identify the dispersed phase and the emulsifier in milk. 1

(b) CO_2 (g) is much more soluble in NaOH (aq.) than it is in water. Can you explain why? 2

(c) 10 ml of HCl solution gave 0·1435 g of AgCl when treated with excess of $AgNO_3$. Find the normality of the acid solution. [Ag = 108] 3

(d) The two acids H_2SO_4 and H_3PO_4 are neutralized separately by the same amount of an alkali when sulfate and dihydrogen orthophosphate are formed respectively. Find the ratio of the masses of H_2SO_4 and H_3PO_4. [P = 31] 4

4. (a) An element has its maximum and minimum oxidation states $+m$ and $-m$ respectively and it does not have the possibility of undergoing disproportionation in any of its compounds. What is the value of m? 2

(b) (i) A current of 5A is passing through copper wire. Calculate the number of electrons passing through a point per second. [$e = 1{\cdot}6 \times 10^{-19}$C] 1

(ii) Mention **two different** ways of drawing the following equilibrium towards right : 2

$$CH_3COOH + CH_3CH_2OH \xrightleftharpoons{H^{\oplus}} CH_3COOC_2H_5 + H_2O \text{ (all are liquids).}$$

(c) The amount of electricity which releases 2·6267 g of gold from a gold salt is same as that which dissolves 1·26 g of copper from copper anode during the electrolysis of copper sulphate solution. What is the oxidation number of gold in the gold salt? [At. wts. of Cu = 63, Au = 197]. 5

5. (a) Give a reaction where water acts as an oxidising agent. 1

(b) How will you separate CO_2 and SO_2 from their mixture? 2

(c) (i) What is Haber catalyst in ammonia synthesis?

(ii) What is autocatalysis? 1+1

(d) Fill in the blanks :

$$\underset{(A)}{\underline{\text{A K-salt}}} \xrightarrow{\Delta} \underset{(B)}{\underline{\qquad}} + Cr_2O_3 + \underset{(C)}{\underline{\qquad}}$$

$$K_2Cr_2O_7 + H_2SO_4 + \underset{(D)}{\underline{\qquad}} \longrightarrow K_2SO_4 + Cr_2\,(SO_4)_3 + H_2O + \underset{(C)}{\underline{\qquad}}$$

$$KClO_4 \xrightarrow{\Delta} \underset{(E)}{\underline{\qquad}} + \underset{(C)}{\underline{\qquad}}$$

Give balanced equations. 5

6. (a) What type of salts are— Na_2HPO_3 and NaHS? 1

(b) Why pure HI kept in a colourless bottle acquires a brown colour after sometime? 1

(c) (i) Describe with equations what happens when carbon is heated with concentrated sulfuric acid.

(ii) State how will you remove the reducing gas from it. 1+1

(d) What products are obtained when white phosphorous is boiled with caustic potash solution? 2

(e) Give an example for each of the following : 4

(i) oxidising capacity of fluorine, (ii) bleaching action of chlorine,
(iii) reducing property of iodine, (iv) reducing property of hydraiodic acid.

7. (a) Which of the following metal cannot be extracted by the smelting process? 1

Al, Zn, Fe, Pb.

(b) Arrange the following substances in order of increasing carbon content : 1

wrought iron, cast iron, steel.

(c) Write down the electrodes, electrolyte and electrode reactions for extraction of aluminium from pure Al_2O_3. 3

(d) (i) What is cryolite? State its use. 1

(ii) What happens when :

(A) Iron is heated at 100°C with a mixture of finely divided aluminium and aluminium oxide in a reducing atmosphere of hydrogen? 1

(B) A mixture of aluminium oxide and coke heated in a current of chlorine? 1

(iii) A white powdered compound absorbs moisture from the air but is not deliquescent. It does not dissolve completely in water. On reacting with mineral acid produces a gas while decolorizes vegetable colours by oxidation. Name the compound with the relevant reactions. How the compound is manufactured? 2

8. (a) Find the structure of the hydrocarbon that produces one mole each of ethanedial and butanedial on ozonolysis. 2

(b) Devise a scheme for the synthesis of n-butane using CH_3I as the only carbon source. Can you employ the reactions in your scheme to synthesize propane in fairly pure state? Explain. 4

(c) (i) How many monochloro products would you expect when 2-methylbutane is chlorinated? Write their structures and IUPAC names. One of them may have stereoisomer. Indicate it. 3

(ii) Which of the isomer(s) will not give one product only on dehydrohalogenation with alcoholic KOH? 1

9. (a) Name the reagent by which most aldehydes can be made to undergo Cannizzaro type reaction. Give the equation of the reaction also. 1

(b) What happens when an alkyl nitrile reacts with a Grignard reagent followed by addition of dilute acid to the reaction mixture? Mention the relevant equations. 2

(c) State what happens when ammonium acetate is heated with glacial acetic acid and the product thus formed is heated with bromine and caustic potash solution. 3

(d) A fuming organic liquid *A* rapidly reacts with ethanol to give a liquid *B* and a gaseous product *C*. An aqueous solution of *C* gives a curdy white precipitate with $AgNO_3$ solution. The precipitate is soluble in dilute aqueous ammonia but insoluble in dilute nitric acid. $LiAlH_4$ reduction of *B* generates ethanol as the only product. Identify *A*, *B* and *C* and give equations for the reactions. 4

10. (a) When phenol reacts with phosphorus pentachloride minor amount of chlorobenzene is formed. What is the major product? Write down its structure. 2

(b) How many aniline be (i) monobrominated and (ii) mononitrated? Show the steps. 4

(c) An aromatic compound *A* containing one oxygen atom has 76·6% *C* and 6·38% hydrogen. It is soluble in aqueous caustic alkali and gives characteristic colour with $FeCl_3$ solution. When treated with NaOH and CO_2 at 140°C under pressure *A* furnishes *B* which after acidification gives *C*. Acetylation of *C* gives *D* which is used as a pain killer. Identify *A*, *B*, *C* and *D*. Give reasons in favour of your answer. 4

H. S. CHEMISTRY : 2004

First Paper

Group — A

Answer any *four* questions.

1. (a) State the law of reciprocal proportion and explain it with a suitable example. 2+2

(b) Prove that the molecular weight of a gas is twice its vapour density. 3

(c) The weight of 175 ml of a diatomic gaseous element of 0°C and 4 atmosphere pressure is 1·0 g. Calculate the weight of one atom of the gas in grams. 3

2. (a) State Charles law for gases. What is absolute zero? Why is it so called? Is it possible to verify it experimentally? Explain. 1+1+1+1

(b) State Graham's law of diffusion. Give an example of its application. 2+1

(c) 200 ml of a mixture of CO and CO_2 are passed through red hot coke. After the reaction is over, the volume becomes 320 ml measured at the same temperature and pressure. Find the composition of the original mixture. 3

3. (a) Justify or contradict the statement with an example—the equivalent weight of an element is constant. 2

(b) What is solubility curve? Mention any two main uses of it. 2+1

(c) The oxides of two metals *A* and *B* are isomorphous. The atomic weight of *B* is 43·5 and the vapour density of its chloride is 75. 1·02 g of the oxide of *A* contains 0·48 g oxygen. Calculate the atomic weight of *A*. 4

(d) The molecular weight of H_3PO_3 is 'M'. What is its equivalent weight? Give the reason. 1

4. (a) State with suitable examples the Arrhenius concept of acids and bases. Explain with examples what are strong and weak acids. 2+2

(b) Explain why an aqueous solution of $NaHCO_3$ is alkaline. 2

(c) 10·12 g of a saturated aqueous solution of Na_2CO_3 at 27°C required 80·00 ml of (N/2) HCl for complete neutralisation. Calculate the solubility of Na_2CO_3 at 27°C. 4

5. (a) What do you mean by 'chemical equilibrium'? Why is it called dynamic equilibrium? 2

(b) Write down the expression for equilibrium constant K for the following reaction using molar concentration and partial pressure.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad 2$$

(c) Sulphur dioxide is catalytically oxidised by oxygen of air following the equation.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + Q \text{ cals}$$

Apply Le Chatelier's principle to find out the effect of temperature and pressure on the yield. Justify the use of optimum temperature for this reaction in the contact process. Why catalyst is used in this reaction? 1+1+1+1

(d) "For a given ideal gas, the ratio V/T at constant pressure is same for different amounts of the gas"—explain with reasons whether the statement is true or false. 2

6. (a) Establish the relation F/N = e (the terms have their usual meanings). 2

(b) Explain with reasons : 2×2

(i) Same products are obtained when dilute sodium hydroxide solution and dilute sulphuric acid are separately electrolysed with platinum electrodes.

(ii) Pure liquid hydrogen chloride and pure water are both bad conductors of electricity but an aqueous solution of hydrogen chloride is an electrolyte.

(c) If the total volume of H_2 and O_2 at the electrodes during the electrolysis of acidulated water is 33·6 ml at NTP, calculate the quantity of electricity used. If the current is passed for 38·6 sec. what is the strength of current in amperes? 4

Group — B

Answer any *four* questions.

7. State, with equations, how you will prepare (attempt any *five* questions) 2×5=10

(a) phosphorus from bone-ash.

(b) borax from colemanite.

(c) carbon monoxide from oxalic acid.

(d) pure nitrogen from a mixture of nitrogen and oxygen.

(e) sodium nitrite from sodium nitrate.

(f) sulphur dioxide from concentrated sulphuric acid.

8. (a) Write the chemical identity of the following compounds : $\frac{1}{2} \times 6$

dry ice, water gas, bleaching powder, Nessler's reagent, borax, nitrolim.

(b) Describe, with equations, the reducing properties of hydrogen peroxide and sulphur dioxide. 3

(c) Write what is 'Merck's perhydrol'. 1

(d) Express the strength of '10-volume hydrogen peroxide' in gms/litre. 3

9. Answer any *five* questions :

(a) Write how will you detect chloride radical and sulphide radical in the laboratory by wet tests. 1+1

(b) Write how boric acid may be detected. 2

(c) Write, with equation, how the white colour of blackened oil-paintings can be restored with the help of hydrogen peroxide. 2

(d) Write, with equations, how the ingredients of a binary mixture of sulphur and iodine can be separated. 2

(e) Write, with equation, how the permanent hardness of a sample of hard water can be removed with the help of 'calgon'. 2

(f) Write, with equation, the 'ring-test' of nitrate radical. 2

10. (a) Describe, with equations, the process of manufacture of nitric acid from ammonia. 4

(b) On heating an orange solid (A), a green residue (B), a colourless gas (C) and water were produced. (C), on passing over hot magnesium metal, produced a solid (D). (D) on hydrolysis gave a pungent gas (E). (E), on passing over hot copper oxide, produced (C) again. Identify (A), (B), (C), (D) and (E). Explain the changes with chemical equations. 4

(c) Write how ammonia can be converted to urea. 2

11. Write with chemical equations, what happens when (attempt any *five*) 2×5

(a) phosphine gas is passed through an aqueous solution of copper sulphate.

(b) hydrogen sulphide gas is passed through an acidified solution of potassium permanganate.

(c) a mixture of sodium chloride, manganese dioxide and concentrated sulphuric acid is heated.

(d) ozone is passed through an acidified solution of stannous chloride.

(e) zinc metal is reacted with cold and very dilute aqueous solution of nitric acid.

(f) an aqueous solution of sulphur dioxide is heated in a closed container at 150° and cooled subsequently.

12. Show reasons, why (attempt any *five*) 2×5

(a) nitrogen forms only the trichloride but phosphorus forms both the trichloride and the pentachloride,

(b) NH_3 is more basic than PH_3,

(c) aqueous solution of borax is alkaline,

(d) BaO_2 is a peroxide but MnO_2 is not a peroxide,

(e) KHF_2 exists but not $KHCl_2$,

(f) $KClO_3$ alone cannot produce oxygen below 630°C but an intimate mixture of $KClO_3$ and MnO_2 produces oxygen smoothly at a much lower temperature.

JT. ENT. CHEMISTRY : 2004

1. (a) A monoatomic anion of unit charge contains 45 neutrons and 36 electrons. Find the atomic number, mass number of the ion with its identification. 2

(b) (i) Write the ground state electronic configuration of Cu^{+1}, N^{-3}, Cr.

(ii) Why are there no possibilities of 2d and 3f orbitals? 3

(c) Equal amounts of two samples of carbon were burnt and the radioactivities of CO_2 formed were measured. The activities were 2100 and 1400 counts per week respectively. Find the age difference of the samples. In showing radioactivity, how does C^{14} nucleus change? [$t_{1/2}$ for C^{14} = 5600 yrs.] 5

2. (a) What is kg-mole? Find out the total number of electrons in a kg-mole of O_2. 2

(b) State with reasons : 4

(i) Which is more acidic—anhydrous HCl or aqueous HCl?

(ii) Which is more polar—CO_2 or N_2O?

(iii) Which is more volatile—*ortho*-nitrophenol or *para*-nitrophenol?

(iv) Which is more soluble in water—ethyl alcohol or dimethyl ether?

(c) A mixture of FeO and Fe_3O_4 when heated in air to constant weight gains 10% in its weight. Find the composition of the original mixture. (Fe = 56] 4

3. (a) On which factors will the rate of diffusion of a gas depend? 1

(b) Find out the ratio of equivalent weight of $H_2C_2O_4, 2H_2O$ as an acid and its equivalent weight as a reductant. 2

(c) Classify the following as acid or base according to Bronsted-Lowry theory and name their corresponding conjugate base or acid : 3

(i) $\ddot{N}H_3$. (ii) CH_3COO^-, (iii) H_3O^+, (iv) H^-, (v) HOO^-, (vi) $S_2O_8^{-2}$.

(d) A sample of mixed alkali contains NaOH and Na_2CO_3 is titrated in the following two schemes :

(i) 10 ml of above mixture requires 8 ml 0·1 (N) HCl by using phenolphthalein.

(ii) 10 ml of above mixture requires 10 ml 0·1 (N) HCl by using methyl orange.

Calculate the ratio of the weight of NaOH and Na_2CO_3 in the sample mixture. 4

4. (a) The equilibrium constant for the following reaction : $A_2 + B_2 \rightleftharpoons 2AB$ is K_p. What will be the equilibrium constant for the reaction, $AB \rightleftharpoons \frac{1}{2} A_2 + \frac{1}{2} B_2$? [A, B and AB, all are gaseous] 1

(b) What is a catalyst poison? Give an example with an appropriate reaction. 2

(c) Balance the following equations by oxidation number method : 3

(i) $S + HNO_2 \rightarrow SO_2 + NO_2 + H_2O$.

(ii) $P_4 + NaOH + H_2O \rightarrow PH_3 + NaH_2PO_2$.

(d) A 100 W, 110 V incandescent lamp is connected in series with an electrolytic cell containing $CdSO_4$ solution. What mass of cadmium will be deposited at the cathode after 4 hours of electrolysis? Calculate gram equivalent of acid that will be formed. [Cd = 112·2] 4

5. (a) Is it possible to remove completely by boiling the temporary hardness due to $Mg(HCO_3)_2$? 2

(b) Calculate the molarity strength of a sample of H_2O_2 solution marked "30 volume". 3

(c) **A** and **B** are two pungent colourless gases, highly soluble in water. The two gases react to form **C** which is solid. At high temperature the gas **A** reacts with sodium to produce a solid **D** and hydrogen. **A** forms a white precipitate **E** with $ZnSO_4$ solution and **E** is soluble in excess of **A** by forming **F**. Identify **A, B, C, D E** and **F** and give the chemical reactions. 5

6. (a) Moist blue litmus paper first turns red and then becomes colourless when introduced into a gas jar of chlorine. Explain. 2

(b) How would you separate the ingradients from a mixture of H_2S and SO_2? 2

(c) Explain why H_3PO_3 is a dibasic acid while H_3PO_4 is a tribasic acid. 2

(d) (i) How P_2H_4 free PH_3 is obtained from white phosphorus?

(ii) How pure chlorine gas is obtained at room temperature? 4

7. (a) During electrolysis of $CaCl_2$, Cl_2 is liberated at the anode, but it never reacts with the calcium deposited on cathode.—Why? 2

(b) How Cu_2O act as both oxidant and reductant, explain with proper reactions showing the changes of oxidation numbers in each example. 3

(c) A white solid **A** when heated with dilute HCl gives out a gas **B** which smells of rotten egg and forms a colourless solution **C**. **C** reacts with NH_4OH solution without any visible change. When NaOH solution is gradually added to **C** it first forms a white precipitate **D** which dissolves in excess of the reagent. However if the gas **B** is again passed through this final solution the white solid **A** is reprecipitated. Identify the compound **A** and give the necessary equations. 5

8. (a) Which one of the following has the maximum number of π-bonds—propyne, butadiene, benzene? 1

(b) A saturated hydrocarbon **A** was found to have vapour density 36. It forms only single monochloro substitution product. Suggest **A**. 2

(c) Draw the structures of isomeric ethers possible with the formula $C_5H_{12}O$. 3

(d) An organic compound **A** (molecular formula $C_4H_{10}O$) reacts vigorously with acetyl chloride and respond to iodoform test. When passed over hot alumina, **A** is converted to another compound **B** (C_4H_8) which on ozonolysis gives only one aldehyde. Identify **A** and **B** with reasons. 4

9. (a) Convert the following in one step : 1

(i) $>C = O \rightarrow >CH_2$.

(ii) $CH_3CO_2H \rightarrow ClCH_2CO_2H$.

(b) How will you prepare pure and anhydrous formic acid from an aqueous solution of the acid? 2

(c) **A** and **B** are two isomeric compounds of formula, C_2H_5ON. **A** on treatment with P_2O_5 gives **C**. Both **A** and **C** on alkaline hydrolysis evolve NH_3. **B** can be easily prepared from acetaldehyde. Write the structures of **A, B** and **C**, and formulate the reactions. 3

(d) An organic compound liberates CO_2 on reaction with sodium bicarbonate. When its sodium salt is heated with sodalime, the first member of alkane series is produced. When its calcium salt is dry distilled, the first member of ketone series is produced. Identify the compound and write down the reactions. How can you convert its sodium salt into an alcohol in one step? 4

10. (a) How can you demonstrate that the double bonds of benzene is somewhat different from that of olefines? 1

(b) What is compound **A** in the following reaction?

$$C_6H_5\overset{+}{N}_2\overset{-}{Cl} + KCN \xrightarrow{CuCN} A$$

How do you prepare an isomer of **A** from aniline? 2

(c) What happens when a mixture of phenol and phthalic anhydride in 2 : 1 mole ratio is heated with conc. H_2SO_4? What do you expect if the product is treated with aqueous Na_2CO_3 solution and why? 3

(d) Identify the lettered compounds :

$$C_6H_5CH_2OH \xrightarrow[\Delta]{SOCl_2} A \xrightarrow[ether]{Mg} B \xrightarrow{CH_3CHO} C + D$$

Both **C** and **D** respond to iodoform test. **C** on oxidation gives an acid **E** having neutralisation equivalent of 122. **D** on similar oxidation gives another acid **F** which may form two mono nitro derivatives. 4

NOTES